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Adaptation of a flow-through leaching procedure for Mg/Ca paleothermometry

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[1] Mg/Ca ratios in planktonic foraminifera reflect calcification temperatures and are thus useful for sea surface temperature (SST) reconstructions. Despite the obvious utility of this paleoceanographic tracer, problems of dissolution, gametogenic calcification, and contaminant phases have thus far limited confidence in Mg/Ca-based reconstructions. Here we show strong evidence of Mg heterogeneity in foraminiferal calcite by sequentially measuring the composition of different forms of calcite (ontogenetic, gametogenic, diagenetic) in the same shells, while monitoring and removing contaminant phases. A new flow-through method combines chromatographic technology and inductively coupled plasma mass spectrometry (ICP-MS) in a series of cleaning and dissolution reactions monitored continuously with time-resolved analysis (TRA). This combination of slow, controlled dissolution and TRA provides a complete elemental description of contaminant phases and sorts the cleaned calcium carbonate based on dissolution sensitivity. Examination of partially dissolved shells with electron microscopy suggests that the flow-through method simulates the natural dissolution sequence and effectively separates the different calcite domains within a single foraminiferal shell. Heterogeneity of Mg/Ca in foraminiferal calcite is clearly demonstrated in flow-through analysis. Foraminiferal shells have initially high Mg levels that decrease steadily throughout dissolution. Later dissolution yields lower Mg/Ca, which is likely due to a combination of subsurface calcification and biomineralization effects. Mg/Ca ratios from the most dissolution-sensitive (high-Mg) portions of surface-dwelling species in core tops are used to calculate calcification temperatures. A comparison of late Holocene core top data with World Ocean Atlas SST data indicates that the flow-through method does yield viable SST estimates. Furthermore, a depth transect in the eastern tropical Pacific suggests that this approach provides the opportunity to extract initial calcification temperatures despite partial dissolution of foraminiferal shells.

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1. Introduction

[2] Mg is a conservative element in the world's oceans with a residence time of ~13 million years [*Broecker and Peng*, 1982]. Despite a nearly constant Mg/Ca ratio in seawater, Mg distribution in biogenic calcite is heterogeneous [*Bender et al.*, 1975]. This heterogeneity may be attributed to the differences in the Mg partition coefficients between inorganically and biogenically precipitated calcite [*Katz*, 1973; *Mucci and Morse*, 1990], as well as the large range of temperatures over which calcification occurs [*Nürnberg et al.*, 1996]. A discrepancy between relatively high Mg/Ca predicted by thermodynamics and low Mg content measured in foraminifera suggests that Mg substitution is physiologically controlled.

[3] Evidence from recent laboratory cultures [*Nürnberg et al.*, 1996; *Lea et al.*, 1999] and core top studies [*Hastings et al.*, 1998; *Lea et al.*, 2000; *Nürnberg et al.*, 2000] of different species of foraminifera has identified temperature as a primary environmental controlling factor on Mg/Ca. Other parameters, such as light, nutrient levels, and growth rate, may also affect Mg substitution in biogenic calcite [*Delaney et al.*, 1985; *Nürnberg et al.*, 1996; *Lea et al.*, 1999], but appear to be less important than temperature. For example, salinity effects are relatively minor, and have only proven significant for large salinity changes on the order of 10‰, which are highly unrealistic for the open ocean over timescales of paleoceanographic interest (10^4–10^5 years).

[4] Several studies have shown evidence of Mg heterogeneity in foraminiferal tests [*Brown and Elderfield*, 1996; *Nürnberg et al.*, 1996; *Jha and Elderfield*, 2000], but there is still uncertainty about the mechanisms responsible for this heterogeneity. In addition to environmental variables (i.e., temperature), physiologically controlled biomineralization processes may regulate Mg distribution in foraminiferal calcite [*Elderfield et al.*, 1996]. In a culture experiment, *Nürnberg et al.* [1996] showed significant differences in the Mg content between ontogenetic and gametogenic calcite. In the case of a culture experiment, which maintains a constant temperature, these differences cannot be attributed to calcification at depth (i.e., lower temperatures). Regardless of the controlling mechanism (physiological versus environmental), Mg/Ca in secondary crust may not accurately reflect the initial calcification temperature that is sought after in paleoceanographic studies. Since gametogenesis can contribute a considerable proportion of the total foraminiferal weight [*Bé*, 1980; *Erez and Honjo*, 1981], it is likely that calculations of calcification temperature based on the Mg/Ca of the whole test are biased by the Mg/Ca of the secondary crust toward subsurface temperatures or by physiological conditions that do not represent primary calcification in near surface waters. In the case of the *Nürnberg et al.* [1996] culture experiment, in which secondary crust showed higher Mg/Ca, this would bias toward a higher calcification temperature. Given our limited understanding of the physiological controls on foraminiferal calcite, we also recognize that the Mg/Ca of primary calcite may not be exclusively related to calcification temperature. Nevertheless, known heterogeneity may be a fatal flaw in the Mg/Ca paleotemperature method, which must be addressed before Mg/Ca can become a fully reliable paleoceanographic tool.

[5] A major problem with applying Mg/Ca paleothermometry to geologic samples is dissolution [*Lohmann*, 1995; *McCorkle et al.*, 1995], both in the water column and in the sediment. Experimentation with artificial seawater indicates that the solubility of pure calcite is influenced by the degree of supersaturation, surface area exposure, and Mg content [*Rushdi et al.*, 1998]. Since high-Mg calcite is more soluble than low-Mg calcite [*Brown and Elderfield*, 1996; *Rushdi et al.*, 1998; *Davis et al.*, 2000], partial dissolution of foraminiferal shells on the seafloor selectively preserves calcite with lower Mg/Ca, biased to reflect colder calcification temperatures. Core top Mg/Ca measurements in planktonic foraminifera confirm this effect; Mg/Ca is correlated with water depth [*Rosenthal and Boyle*, 1993; *Russell et al.*, 1994]. *Lea et al.* [2000] calculated a decrease in Mg/Ca of 12% for each kilometer of water depth for cores in the equatorial Pacific, which translates to a temperature bias of −1.3°C per kilometer for modern conditions.

[6] In the following experiments, we focus on eastern tropical Pacific core top specimens of *Globigerinoides ruber* and *Globigerinoides sacculifer*, which are commonly used in ocean temperature reconstructions because of their near surface habitats. Core top Mg/Ca and $\delta^{18}O$ measurements of *G. ruber* and *G. sacculifer* from Ontong Java Plateau, Ceara Rise, and Sierra Leone Rise depth transects have shown significant dissolution effects [*Rosenthal et al.*, 2000; *Dekens et al.*, 2002]. Others have addressed the dissolution problem in different ways, by applying statistical correction terms to calibration equations based on water depth [*Dekens et al.*, 2002], or by developing dissolution proxies [*Bassinot et al.*, 2001]. Here we address issues of dissolution and shell heterogeneity more directly with an innovative chemical technique that cleans and sequentially dissolves biogenic calcite and thus allows Mg/Ca heterogeneity within shells to be analyzed and better understood.

2. Methods

[7] In previous studies of Mg/Ca in foraminifera, a batch dissolution method has been used. In this method, cleaning is done "offline," and dissolution occurs in a single step prior to analysis. This yields one Mg/Ca value per calcite sample, essentially representing a Ca-weighted average over the entire sample. This method cannot directly assess heterogeneity of Mg within shells. To address this problem, we have applied a new automated flow-through dissolution method [*Haley and Klinkhammer*, 2002] developed for rare earth element (REE) analysis. This method interfaces a customized Dionex Ion Chromatograph (IC) with a VG PQ ExCell quadrupole Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) with Time Resolved Analysis (TRA). TRA generates multiple Mg/Ca measurements per sample, thus providing a high-resolution breakdown of cleaning and dissolution reactions from start to finish.

[8] Flow-through cleaning passes a steady stream of reagents over the calcite sample. In this stream, the calcite is cleaned and then dissolved. The IC system is fitted with an Advanced Gradient Pump (AGP), which precisely regulates the flow (pressure) and eluant concentration, and a Dionex LC25 Ion Chromatography heater to control the temperature of the reactions (here, 80°C). Internal standardization [*Falkner et al.*, 1995] with ^{9}Be and ^{115}In (bracketing the mass range for Mg and Ca measurement) continuously corrects for quadrupole drift. These standards are introduced to the eluate as it flows from the IC into the ICP-MS. $^{25,26}Mg$ and $^{43,48}Ca$ are measured using ICP-MS, and Mg/Ca ratios are calculated from standard curves for each isotope. The method can also be run in a different mode using a fraction collector with the Dionex system. In this mode, the dissolution product is collected in a series of fraction collector tubes, and the standards are added to each tube manually prior to analysis on the ICP-MS. To obtain blank corrections, an empty sample column is run using the same flow-through cleaning and dissolution procedures outlined above. This yields a time-resolved blank correction that is applied to each corresponding time step of the sample data.

[9] We pick approximately 20–30 foraminiferal shells from each sample and place them in 63-μm sieves, where they are cracked just enough to break open the chambers. To remove clays, the shells are sonicated in deionized water and ethanol. The samples are inspected under microscopy for cleanliness, and sonication is repeated if necessary. Clean shells are loaded by hand into disposable sample columns and cleaned and dissolved with the following sequence of reagents using the flow-through method. First, Hydroxylamine HCl ($pH > 9$) is used to remove a coating phase, which contains Mn, Cd, and Mg. During method development, Mg was monitored via TRA during this cleaning step to insure that the contaminant phase had been completely removed [*Haley and Klinkhammer*, 2002]. To remove build-up of elements that may adsorb to the tubing walls (in a high-pH environment), the system is then rinsed with strong acid (1 M HNO_3), bypassing the sample to avoid premature dissolution. Then the sample itself is rinsed with deionized water prior to dissolution. Finally, dilute acid (0.01 N HNO_3) is used to dissolve the sample at a controlled rate. Since the calcite of different foraminiferal species dissolves at different rates, as observed with dissolution in the ocean [*Berger*,

1970], it is sometimes necessary to adjust acid strength (and thus, the dissolution time) accordingly. The acid strength can be adjusted easily via the programmable AGP, which can mix acid and deionized water prior to entering the sample column.

[10] In replicate samples, dissolution proceeds from start to finish in approximately the same amount of time, regardless of sample size, providing evidence that the system is in steady state. The benefit of being in steady state is that cleaning and dissolution reactions are consistent and regulated to a high degree of accuracy, regardless of variability between samples. Standard error of Mg/Ca measurements using the flow-through method is ~2.5%. A more complete description of the analytical details of the method, including comparisons of batch [*Lea et al.*, 1999] and flow-through Mg/Ca results, is available from *Haley and Klinkhammer* [2002].

3. Results and Discussion

3.1. Quenched Dissolution Experiment

[11] Does our flow-through system dissolve different parts of the foraminifera in a way that mimics the natural dissolution process? Foraminifera have complex shells. They tend to calcify in discrete layers, and although the shell is entirely composed of calcite, the layers may take different crystal forms that dissolve at different rates. For example, *Bé and Lott* [1964] illustrate two layers of calcite in living foraminifera from plankton tow samples; in each chamber, two layers are deposited: a thin inner layer and a thicker layer with prismatic crystals oriented perpendicularly to the test surface. The outer lamella envelops the exterior of earlier chambers, making these primary biogenic structures difficult to see in the early chambers. In specimens recovered from water depths of more than several hundred meters, these lamellae are typically covered by a third layer, a calcite "crust" formed of randomly oriented euhedral crystals. *Bé et al.* [1975] refer to these three discrete layers of calcite (in order of decreasing dissolution sensitivity) as the "microgranular layer," the "subrhombic layer," and the "euhedral layer," respectively (or alternatively, the first two layers are "ontogenetic calcite" and the third layer is "gametogenic calcite").

[12] To test whether foraminifera dissolve sequentially in our apparatus as they do on the seafloor, we performed partial dissolution experiments, which were quenched at different stages of dissolution. The partially dissolved shells were then compared visually (using electron microscopy) to naturally dissolved shells from a depth transect of sediment cores. For our partial dissolution experiments, we selected well-preserved shells of *Globigerinoides sacculifer* from the top of multicore MW9720-MC1, recovered from 1775 m water depth on Ontong Java Plateau (1° 29.75′S, 157° 30.20′E). These shells were cleaned ultrasonically (without crushing, so we could see the reasonably complete shells after our experiments), and then subjected to sequential dissolution in our normal online reaction chamber. After partial dissolution, the reactions were quenched with dilute NH_4OH, and the shells were removed and prepared for observation with a CAMECA SX-50 electron microprobe. For comparison, we also observed shells that dissolved naturally on the seafloor, hand picked from the top of multicore MW9720-MC37, recovered from 3707 m water depth on Ontong Java Plateau (0° 00.36′S, 161° 23.28′E). This is the deepest available multicore on Ontong Java Plateau that contains identifiable (although often fragmented) shells of *G. sacculifer*. In cores from deeper sites, we observed only shell fragments, with no identifiable *G. sacculifer*.

[13] Results from our partial dissolution experiments are illustrated in Figure 1. In the top two panels (Figures 1a and 1b), pristine shells taken from 1775 m water depth were cleaned ultrasonically (three times, five minutes each, in ethanol) but otherwise were unprocessed. These panels show all three layers of the test wall. The surface of the interior microgranular layer is smooth (Figure 1a). The exterior of the test shows pitted areas and pores (Figure 1a) that were associated with the bases of spines shed from the living cell. Note especially the complete interior layer and smooth periphery of the pores.

[14] In Figure 1c, cleaned shells were subjected to partial dissolution for one minute, removing about 5% of the total calcite (based on weight loss). Note here the enlargement of the pores, their ragged

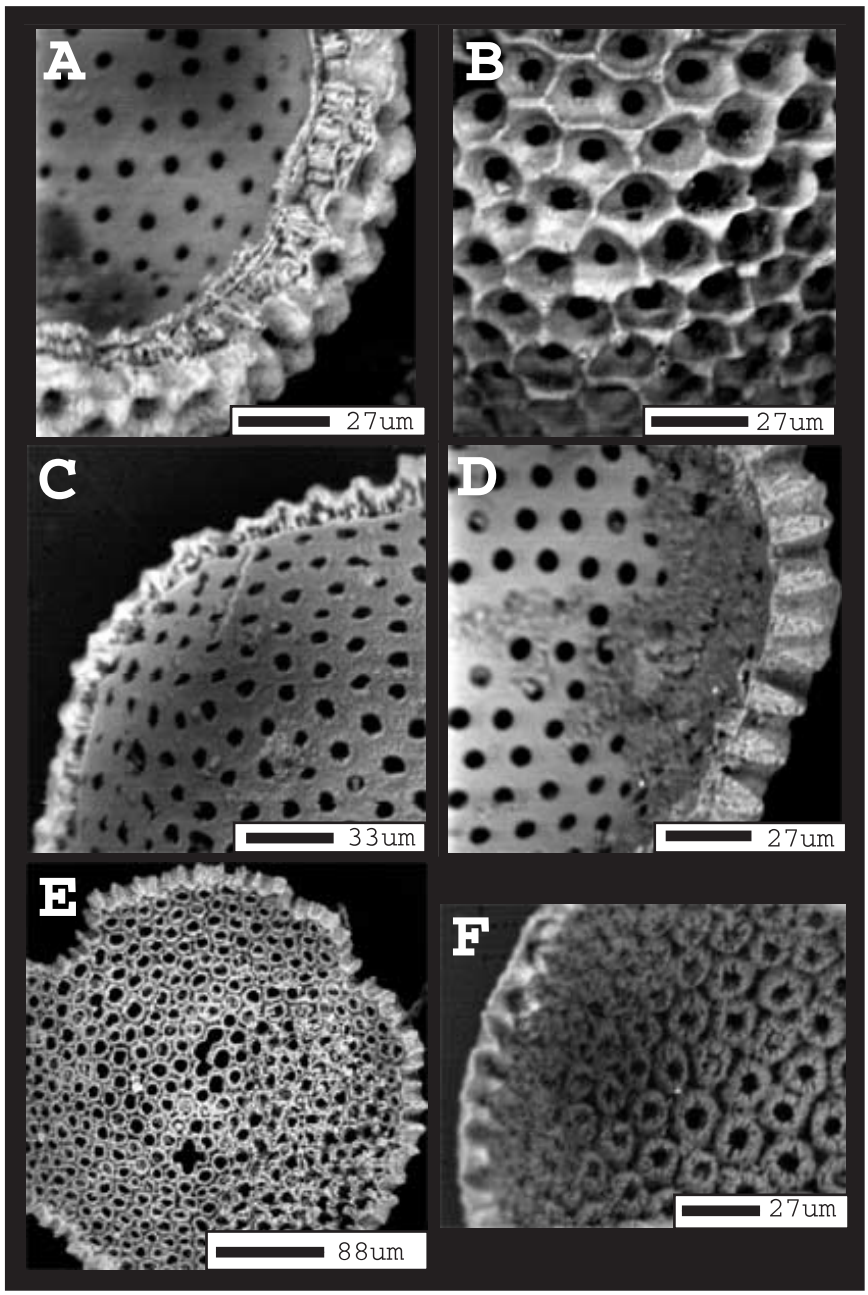

Figure 1. Backscatter scanning electron micrographs of *G. sacculifer* shells to illustrate continuous dissolution in our reaction chamber versus nature: (a) interior and (b) exterior of ultrasonically cleaned shells picked from 1775 m water depth on Ontong Java Plateau (MW9720-MC1: 1° 29.75′S, 157° 30.20′E, 1775 m) (note pristine appearance and interior layers); (c) experiment in which partial dissolution removed ~5% of the total calcite (note enlargement and corrosion of the interior layer around the pores); (d) a relatively complete shell from 3707 m water depth on Ontong Java Plateau (MW9720-MC37: 0° 00.36′S, 161° 23.28′E, 3707 m) illustrating similar interior corrosion on seafloor; (e) experiment in which partial dissolution removed ~60% of the total calcite (note interior layer gone, pores in exterior layer now corroding); and (f) shell fragments from 3707 m water depth illustrating similar removal of interior layer under severe dissolution.

edges, and apparent thinning of the interior layer. This represents early dissolution of the shell, from the inside out. Compare Figure 1c to the seafloor specimen of Figure 1d, a relatively complete shell picked from 3707 m water depth, which we cracked open to observe the interior; note similar thinning and apparent corrosion of the interior microgranular layer.

[15] In a more severe dissolution experiment, shells similar to those of Figure 1a were subjected to dissolution for 6 minutes, removing about 60% of the total calcite. In the shell fragments remaining from this dissolution (Figure 1e) note that the interior microgranular layer is essentially gone, and that the exterior layer is now corroding as the pores expand to yield a ''lacy'' appearance. We observed a similar dissolution pattern in naturally dissolved seafloor shell fragments from 3707 m water depth (Figure 1f). Similar to the specimen dissolved in the laboratory, the interior microgranular layer is essentially gone, and the pores are corroding. At greater degrees of dissolution, the shells fragment and become difficult to recognize or pick without falling apart.

[16] The point of this experiment is that the dissolution sequences in our experimental chamber and on the seafloor are quite similar. The early dissolution tends to remove the interior microgranular layer first, and the exterior layers dissolve later. This is important, because it shows that our method does simulate the sequential dissolution process that occurs on the seafloor, chemically sorting genetically distinct layers of calcite. The earliest calcite dissolved appears to be the inner calcite layers, which are most likely to have formed in warmer, near-surface waters. The late-stage dissolution products are the outer layers and ''crusts'' that tend to form in deeper waters.

[17] A similar order of dissolution was found by *Bé et al.* [1975]: first the microgranular layer, followed by subrhombic layer, and finally the euhedral layer (although their illustrations show only exterior surfaces). *Hecht et al.* [1975] argued that foraminifera dissolve from the outside layers in, and from final chambers to the earlier chambers. Our observations of shell interiors at first glance appear to disagree with their suggested order of layers. Note, however, that *Hecht et al.* [1975] examined only the exterior of the shells and illustrated only cases in which 70% or more of the calcite was dissolved from *G. sacculifer*. In this range, which we could call severe dissolution, our results are consistent. We agree that when the outer chambers dissolve, they tend to fragment from the terminal chambers first, but in our observations this only seems to occur after the inner microgranular layer is essentially gone.

[18] Results from these quenching experiments suggest that sequential dissolution discriminates between genetically distinct calcite domains in the foraminiferal shells. We expect that the main reason the inner layers dissolve more quickly is that they have a higher Mg/Ca ratio. If sequential dissolution can sort calcite by its Mg content, we hypothesize that the earliest dissolution we observe is from microgranular layers formed in the warmest (near-surface) water.

3.2. Mg Heterogeneity and Estimates of Calcification Temperature

[19] To test for heterogeneity of the Mg/Ca ratio in foraminifera, we analyzed specimens of *G. ruber* (250–355 μm size fraction) and *G. sacculifer* (355–425 μm size fraction, no terminal sac-like chamber) from core tops in the eastern tropical Pacific. Deeper sites showed some fragmentation of the foraminifera, suggesting that partial dissolution had occurred. In all analyses, Mg/Ca in *G. ruber* and *G. sacculifer* declined as the dissolution progressed (Figure 2), providing strong evidence of Mg heterogeneity in foraminiferal calcite. We show Sr/Ca data for the same samples for comparison. Sr/Ca ratios remain relatively constant throughout the dissolution with the exception of minor (~0.1–0.2 mmol/mol) step changes near the middle to the end of the run that are still not fully understood. *Haley and Klinkhammer* [2002] observed the same trends in Mg/Ca in earlier analyses of *G. sacculifer*. A small spike (~2–3 ppb) in Mg is observed near the beginning of the run in samples ME0005A-15MC *G. ruber* and Y69-106P *G. sacculifer* (Figure 2). This Mg spike occurs during the deionized water flush of the sample column (prior to the

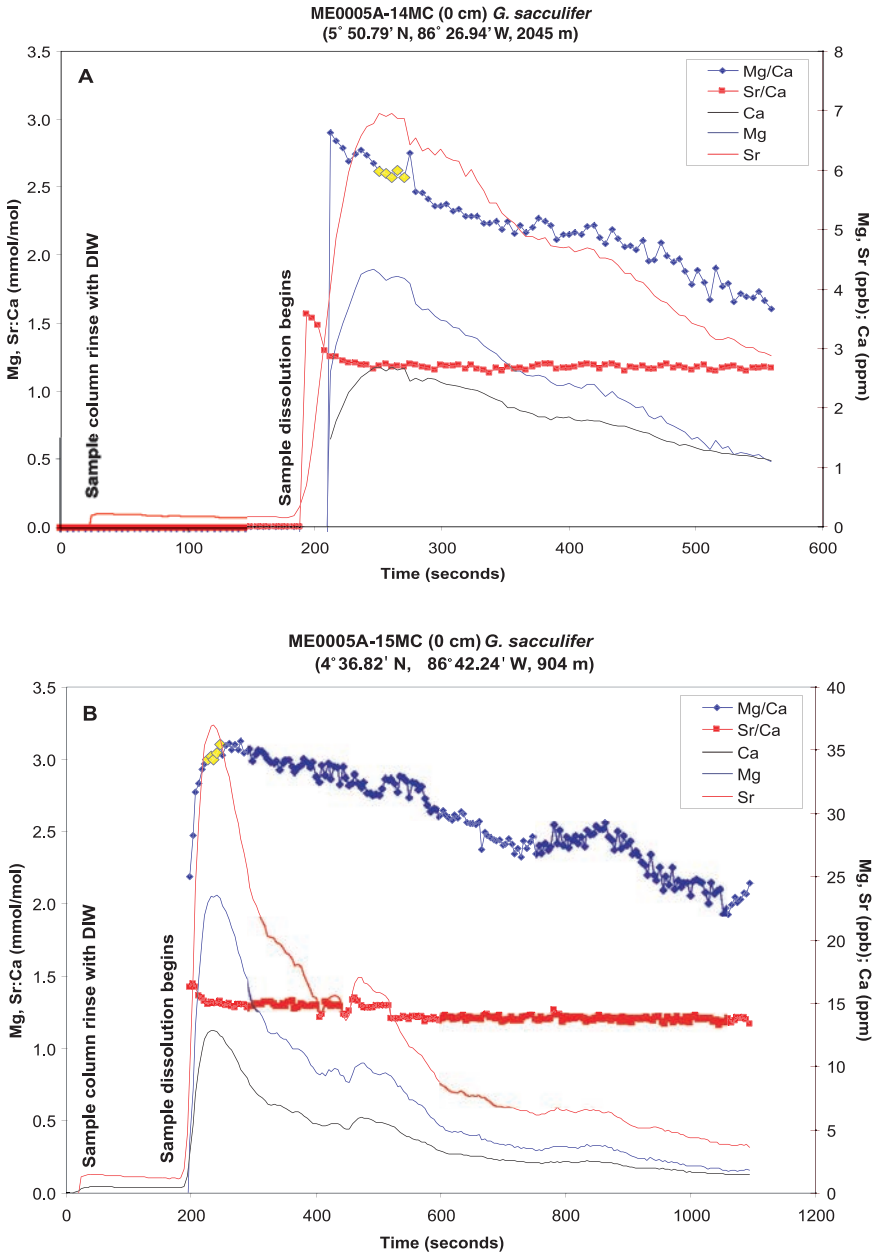

Figure 2. Sequential dissolution of specimens of *G. ruber* and *G. sacculifer* from three cores in the eastern tropical Pacific: (a) ME0005A-14MC (5° 50.79′N, 86° 26.94′W, 2045 m), (b, c) ME0005A-15MC (4° 36.82′N, 86° 42.24′W, 904 m), and (d) Y69-106P (2° 59′N, 86° 33′W, 2870 m). The *x* axis shows time in seconds with time zero representing the start of time resolved analysis, after the sample has been cleaned. The advantage of TRA is demonstrated by the multiple data points produced in the sequential dissolution, which reveals significant heterogeneity in these foraminiferal specimens. The *y* axes show Mg/Ca and Sr/Ca (left axis) and Ca (ppm), Mg (ppb), and Sr (ppb) (right axis). The Sr/Ca in these specimens appears to be homogeneous relative to Mg/Ca. The calcification temperature is calculated based on the average of the five Mg/Ca values associated with the peak in Ca that appears near the beginning of the sequential dissolution. These Mg/Ca values are highlighted in yellow for each site. The Mg/Ca ratios near the ends of the runs are different between sites. This is probably due to incomplete dissolution of the samples, as suggested by Ca and Sr concentrations that are still significantly higher than blank values.

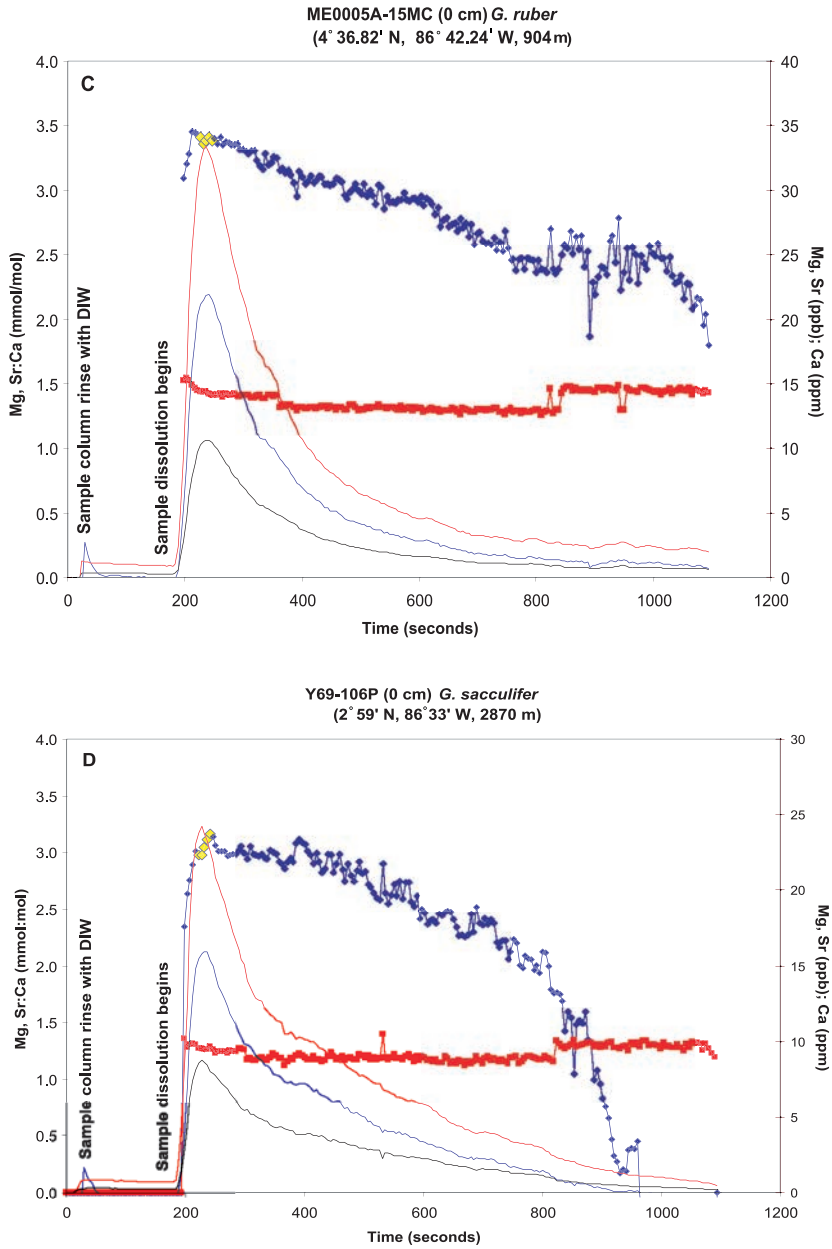

Figure 2. (continued)

introduction of the dilute acid), which removes any remaining traces of contaminant phases from sample cleaning. These small spikes are not accompanied by significant Ca or Sr increases, and thus do not represent significant dissolution of calcite for these shells. Early ramp-up of Mg/Ca occurs in most samples at the beginning of dissolution. This is characteristic of a continuous flow system, and reflects diffusive mixing in the reagent stream, not a true change in shell Mg/Ca. As dilute acid is first introduced to the sample chamber, shell dissolution begins, and there is a gradual displacement of the blank eluate from the sample chamber.

[20] One possible hypothesis to explain the gradual decline we observe in Mg/Ca is incongruent dissolution, in which the $MgCO_3$ that is present as a minor component within the test dissolves at a faster rate than $CaCO_3$. An alternative hypothesis is that the gradual decline in Mg/Ca is a result of

Table 1. Mg/Ca Measurements (Batch/Flow-Through) and Comparison of Batch Versus Flow-Through Mg/Ca-Based Calcification Temperatures for Samples Shown in Figure 2 Using Different Existing Calibration Equations for *G. sacculifer* and *G. ruber*

Sample	Mg/Ca, mmol/mol	Calcification Temperature, °C (Batch Method/Flow-Through Method)[a]			Actual SST,[e] °C (WOA 98)
		Lea et al. [2000][b]	*Nürnberg et al.* [1996][c]	*Dekens et al.* [2002][d]	
ME0005A-14MC (0 cm)					27.7
G. sacculifer	2.16/**2.60**	N/A	19.2/**21.3**	22.3	
ME0005A-15MC (0 cm)					27.4
G. sacculifer	2.63/**3.03**	N/A	21.5/**23.0**	N/A[d]	
G. ruber	2.68/**3.39**	24.6/**27.2**	N/A	N/A[d]	
Y69-106P (0 cm)					26.5
G. sacculifer	2.57/**3.06**	N/A	21.2/**23.1**	24.6	

[a] Calculations based on the flow-through Mg/Ca ratio are in bold.
[b] *Lea et al.* [2000] represents a core top calibration for *G. ruber* (Mg/Ca (mmol/mol) = 0.30exp[0.089 × SST (°C)]) in the equatorial Pacific.
[c] *Nürnberg et al.* [1996] represents a culture calibration for *G. sacculifer* (Mg/Ca (mmol/mol) = 0.39exp[0.089 × T (°C)]).
[d] *Dekens et al.* [2002] represents a core top calibration for *G. sacculifer* (Mg/Ca (mmol/mol) = 0.37exp 0.09[T − 0.36(core depth km − 2.0°C]) from the equatorial Pacific. The *Dekens et al.* [2002] calibration could not be applied to Site ME0005A-15MC because the site is too shallow (904 m); this calibration equation only applies to depths >1.6 km. Also, since this calibration contains a dissolution correction, it was unnecessary to apply it to flow-through Mg/Ca ratios.
[e] Annual average SST for each site taken from World Ocean Atlas (1998).

ordered dissolution of different types of calcite in the test based on Mg content. Earlier experiments by *Haley and Klinkhammer* [2002] showed similar dissolution patterns for *G. sacculifer* from the Ontong Java Plateau. Their measurements of the planktonic foraminifer *Orbulina universa* consistently yielded distinct Mg/Ca "plateaus" that would not likely be generated by incongruent dissolution. Based on these observations and results of our partial dissolution experiment, which demonstrates that sequential dissolution is actually removing different forms of calcite in an ordered sequence (i.e., primary calcite first, followed by secondary calcite), we prefer the latter hypothesis.

[21] Under the assumption that Mg/Ca variability in the shells is primarily related to temperature, we calculated the Mg/Ca temperature using the culture calibration equation of *Nürnberg et al.* [1996] for *G. sacculifer* (Mg/Ca (mmol/mol) = 0.39exp[0.089 × T (°C)]) and a recent core top calibration [*Lea et al.*, 2000] from the tropical Pacific for *G. ruber* (Mg/Ca (mmol/mol) = 0.30exp[0.089 × SST (°C)]; standard error = ±0.6°C). Eventually, we plan to develop species-specific calibrations based on our flow-through technique, but in the meantime we must apply existing calibrations. Since we expect that this method can extract calcification temperatures for a range of calcite concentrations, despite partial dissolution, it would be appropriate to apply culture calibrations, which do not contain built-in dissolution biases. In the absence of a recent culture calibration for *G. ruber*, we applied a recent core top calibration [*Lea et al.*, 2000] that is specific to our study region. However, we recognize that the use of this core top calibration introduces a dissolution bias that does not exist in our Mg/Ca data set.

[22] In this experiment, we calculated "initial" calcification temperatures based on the average of the five Mg/Ca values associated with the peak in Ca that appears near the beginning of the sequential dissolution (Figure 2). We choose these points because if there is high-Mg calcite remaining within a specimen (i.e., it hasn't all been dissolved away), then it should dissolve first, thus corresponding to the Ca peak near the beginning of sequential dissolution. We also calculated the Ca-weighted mean temperature within the entire dissolution, excluding the initial "ramp-up" data. This mimics the value that would be determined in traditional batch dissolutions, assuming that the batch samples were cleaned properly.

[23] Calcification temperatures for *G. ruber* and *G. sacculifer* calculated from the batch versus the flow-through method using different published calibration equations are reported in Table 1. The calcification temperatures calculated from the

flow-through method are consistently higher than those calculated from the batch method. Based on the calcification temperatures derived from the various calibration equations, *G. ruber* calcifies within the mixed layer, whereas *G. sacculifer* seems to calcify within the thermocline at this site, which is consistent with previously published plankton tow data from this region [*Fairbanks et al.*, 1982].

[24] To examine the effects of selective dissolution in seafloor samples, we compared core top Mg/Ca measurements in *G. sacculifer* from continuous and batch dissolution methods at three nearby sites with different water depths: ME0005A-15MC (904 m), ME0005A-14MC (2045 m), and Y69-106P (2870 m) (Figure 3). Oxygen isotope measurements indicate that the multicore tops from 14MC and 15MC are late Holocene in age. The piston core top from Y69-106P is at least mid-Holocene in age. *G. sacculifer* (355–425 μm size fraction) is analyzed in all cores (*G. ruber* is essentially absent in the deeper cores due to dissolution). Core top ME0005A-14MC yields a slightly lower initial Mg/Ca ratio, and immediately shows a steep decline in Mg/Ca during sequential dissolution. The other two cores shown in Figure 3 have a modest plateau in Mg/Ca at the beginning of the dissolution, followed by a steeper decline resembling that of 14MC. Although not the deepest site, it might be that 14MC is showing a larger dissolution effect than the other two cores. The enhanced dissolution in 14MC relative to the deeper site (Y69-106P) may reflect a core top age difference, since the deep Pacific is thought to have undergone a mid-Holocene change in dissolved carbonate ion concentration [*Keir*, 1984]. We would expect that if specimens from 14MC are slightly more dissolved, they would contain less primary calcite, thus yielding less of a "plateau" near the beginning of dissolution, as seen in the other cores. The Mg/Ca pattern in 14MC resembles the latter parts (from ~550 seconds to the end) of the sequential dissolution series in the other two cores (Figure 3). It is likely that the majority (though not all, or we would not obtain an initial Mg/Ca ratio that is so close to that of the other cores) of the early-stage calcite in 14MC has dissolved on the seafloor.

[25] The Mg/Ca ratios near the end of the analysis are notably different between sites (Figures 2 and 3). Lower Mg/Ca ratios may be attributed to lower calcification temperatures, biomineralization effects, or a combination of both. Increased noise occurs in the system after the majority of the sample has dissolved (after the initial peaks in Ca), making the true endpoint (complete dissolution) very difficult to identify. Incomplete sample dissolution would likely explain these differences in the Mg/Ca ratios between sites. We are addressing this problem with further experimentation.

[26] Using the culture calibration equation of *Nürnberg et al.* [1996] for *G. sacculifer* to calculate temperature, we observe a ~1.5–2.0°C discrepancy between batch and continuous temperatures at all three sites shown in Figure 3. Since our primary goal for purposes of estimating paleotemperature is to extract the highest Mg/Ca values remaining in the calcite samples, we are encouraged that the initial temperatures in the core tops from all three sites are quite similar and reflect a depth habitat within the thermocline, which is typical for *G. sacculifer* [*Fairbanks et al.*, 1982]. This suggests that as long as some of the dissolution-sensitive (ontogenetic) calcite is preserved, even in moderately to heavily dissolved samples, it can still be detected via sequential dissolution.

[27] To test the accuracy of the flow-through technique, we compared Mg/Ca-based temperature estimates from *G. ruber* (based on the preliminary temperature calibration of *Lea et al.*, 2000) in the core top ME0005A-15MC with a series of World Ocean Atlas (WOA 98) temperature profiles (annual, seasonal, and flux-weighted averages) from the same site and determined the corresponding calcification depths of this species for batch versus continuous methods (Figure 4). The calcification temperature derived from sequential dissolution was in good agreement (within 0.2°C) with WOA 98 SST data, and corresponded to a calcification depth range of ~0–20 m, which is typical for *G. ruber*, a mixed layer-dwelling organism [*Fairbanks et al.*, 1982; *Faul et al.*, 2000]. In this experiment, ~75–80% of the calcite had a Mg/Ca ratio consistent with mean annual temperature in the upper ~30 m. The remaining calcite had a Mg/

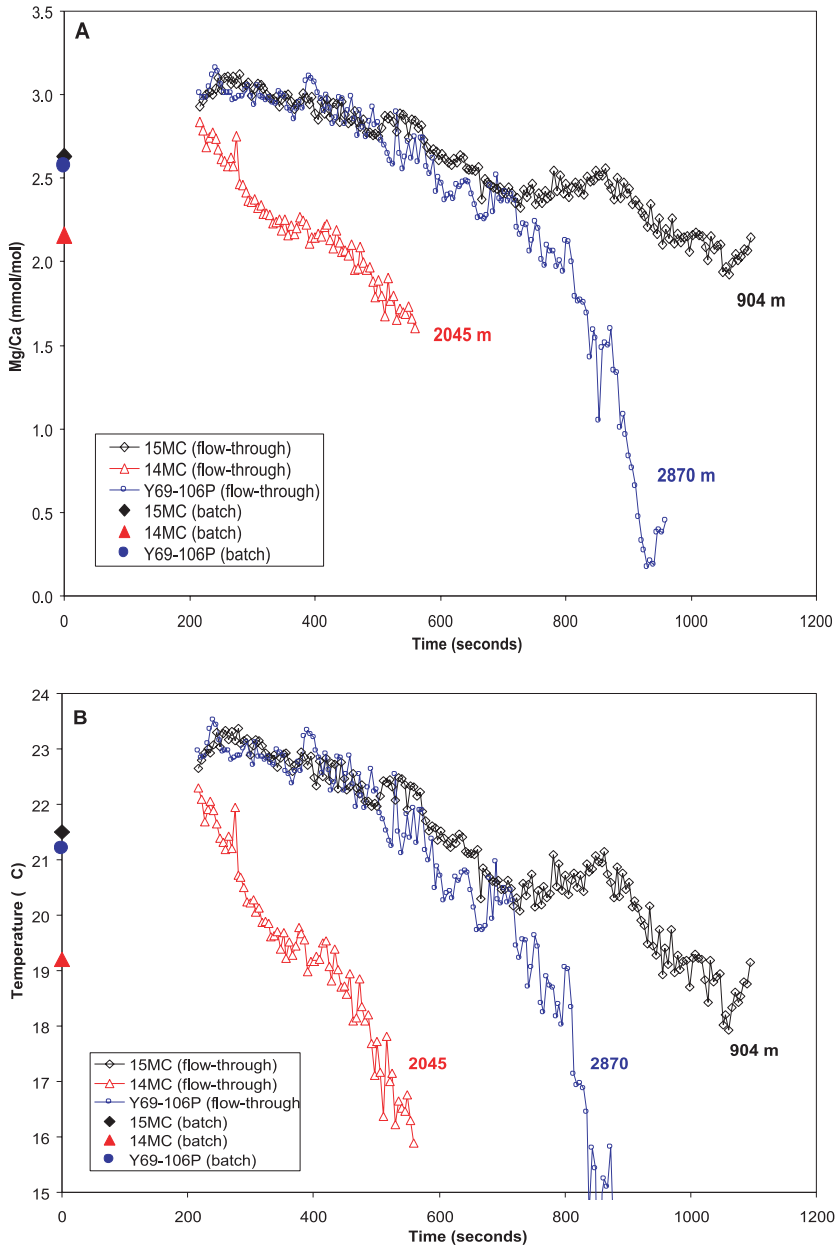

Figure 3. Depth transect showing (a) Mg/Ca and (b) calcification temperatures from *G. sacculifer* for batch versus flow-through in three cores from the eastern tropical Pacific: ME0005A-15MC (4° 36.82' N, 86° 42.24' W, 904 m), ME0005A-14MC (5° 50.79′N, 86° 26.94′W, 2045 m), and Y69-106P (2° 59′N, 86° 33′W, 2870 m). Mg/Ca was converted to calcification temperature using the culture calibration equation of *Nürnberg et al.* [1996] for *G. sacculifer* (Mg/Ca (mmol/mol) = 0.39exp[0.089 × T (°C)]). The batch dissolution values (large symbols on the *y* axis) were obtained by calculating a Ca-weighted average for each sample.

Ca ratio consistent with calcification between 30–50 m. The Ca-weighted "batch" SST estimate of 25.9°C was within the range of that calculated by *Lea et al.* [2000] for this region, and corresponded to a depth of ~35 m, which lies within the thermocline at this site. This lower SST estimate may reflect the contribution of secondary calcite. There is also a bias associated with applying a core top calibration to these data, since the "initial" Mg/Ca ratios used in our temperature calculation do not contain the dissolution effect that is inherent in a core top calibration. Therefore, our SST estimates

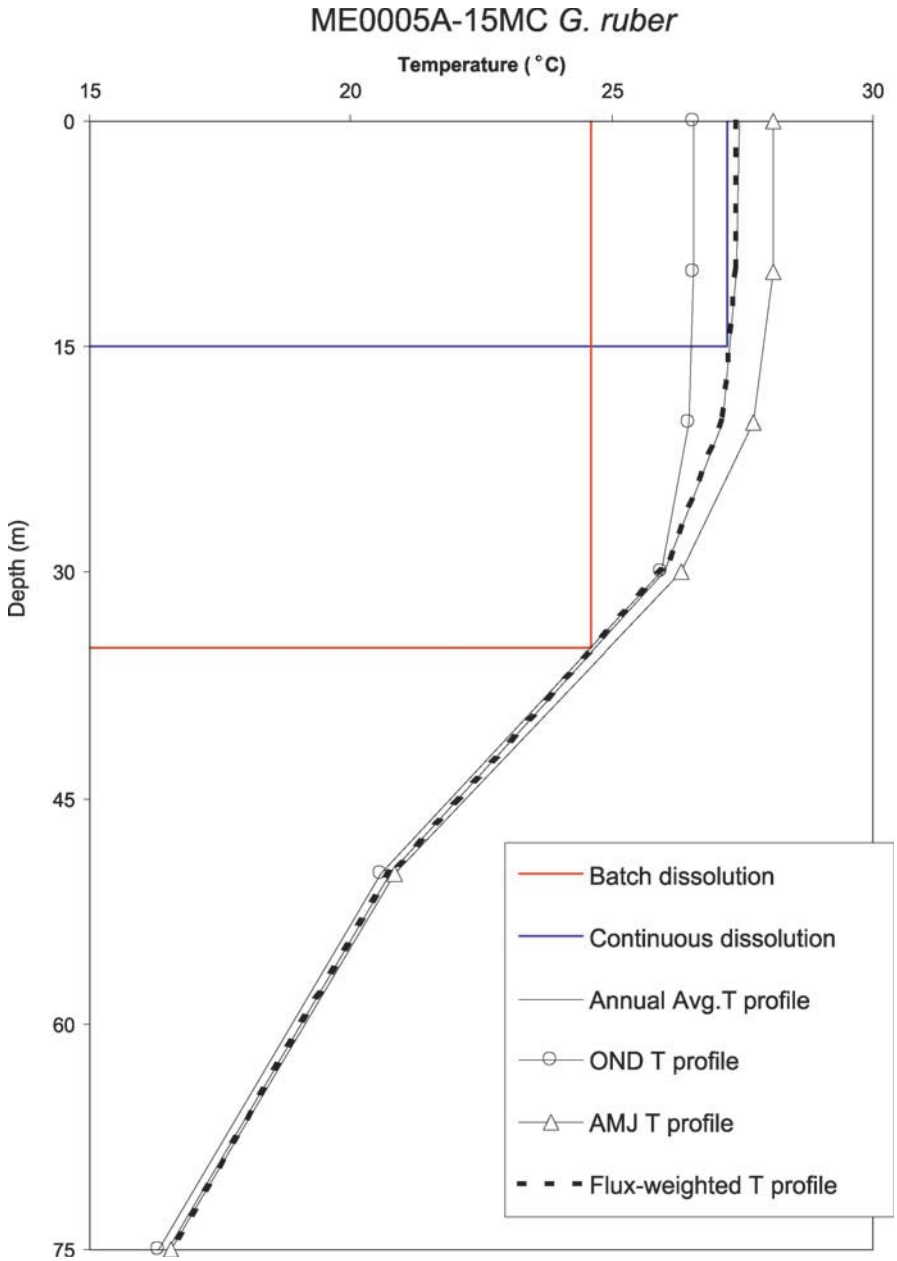

Figure 4. Comparison of batch and continuous Mg/Ca-based temperature estimates for *G. ruber* from a late Holocene Cocos Ridge core top (ME0005A-15MC, 4°36.82′N, 86°42.24′W, 904 m) against World Ocean Atlas (1998) temperature profiles. The blue line represents the initial Mg/Ca values obtained during sequential dissolution (see text for explanation of calculations). The red line represents the batch (Ca-weighted average) dissolution Mg/Ca value. The annual average temperature profile is encompassed by the warmest (April/May/June, or AMJ) and coldest (October/November/December, or OND) seasonal profiles, so as to demonstrate the potential error associated with seasonal variability in this region. The thick black dotted line represents the flux-weighted temperature profile, which is based on the seasonal flux of *G. ruber* in the Panama Basin region (data from *Thunell et al.* [1983]) (see Figure 5). When seasonal variability is taken into account, the calcification depth of *G. ruber*, as predicted by the batch dissolution, is 30 ± 1 m, and the continuous dissolution predicts a calcification depth of 10 ± 10 m. Even when seasonality is taken into account, the continuous method still predicts *G. ruber* calcification within the upper 20 m.

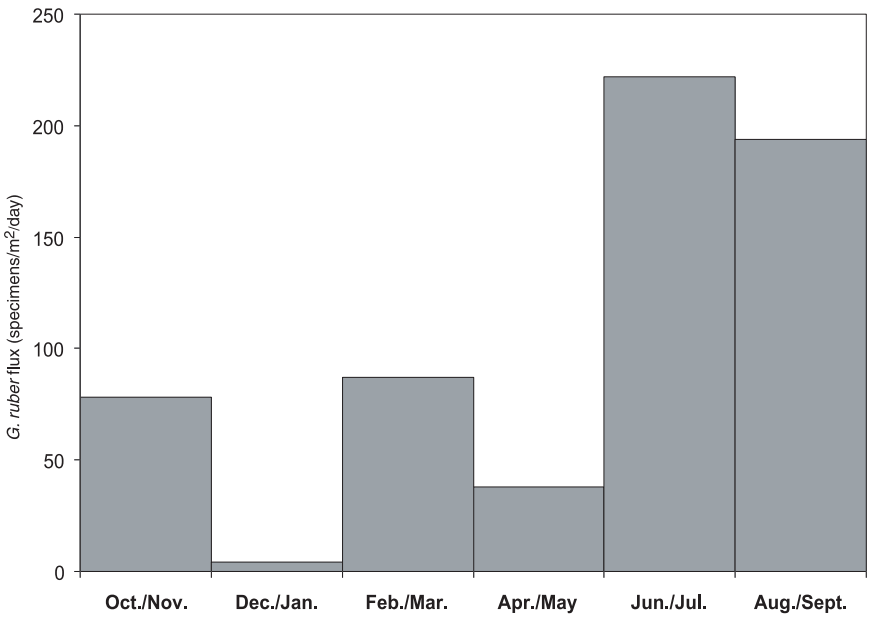

Figure 5. Seasonal flux data from *Thunell et al.* [1983] for *G. ruber* from a sediment trap at 890 m in the Panama Basin region (5° 21′N, 81° 53′W). Foraminiferal specimens are from the 250–500 μm size fraction. These flux data were used to calculate the flux-weighted temperature profile in Figure 4.

from *G. ruber* are probably slightly higher than the true calcification temperatures (also see Table 1).

[28] These results are not significantly affected by seasonality at the study site. Despite seasonal upwelling, the seasonal SST range (shown in Figure 4) in this region is only ~1.5°C (ranging from a low of ~26.5°C in October/November/December, to a high of ~28°C in April/May/June) owing to a strong, shallow pycnocline that hinders vertical mixing, and there is essentially no seasonal variability at depths greater than 30 m (WOA 1998). Previous studies [*Curry et al.*, 1983; *Thunell et al.*, 1983; *Thunell and Reynolds*, 1984] have documented seasonal changes in foraminiferal flux in the Panama Basin region (Figure 5). The seasonal fluxes for *G. ruber* were used to calculate a flux-weighted temperature profile in Figure 4, which is essentially identical to the annual average temperature profile.

4. Conclusions

[29] The flow-through leaching procedure allows us to directly observe heterogeneity of Mg/Ca in biogenic calcite, and addresses issues of contaminant phases and dissolution in the measurement of Mg/Ca. Multiple cleaning experiments monitored with TRA have enabled us to optimize the system for complete removal of contaminant-phase Mg prior to dissolution. Preliminary experiments suggest that 1) The flow-through leaching method closely mimics seafloor dissolution, effectively separating different calcite domains (primary versus secondary) based on Mg content; 2) Mg distribution in foraminiferal calcite is heterogeneous with primary calcite yielding a higher Mg content than secondary calcite; 3) The flow-through leaching method yields reliable estimates of calcification temperature, despite partial dissolution of foraminiferal shells. Although we cannot presently rule out the incongruent dissolution hypothesis, the body of evidence shown here strongly favors our hypothesis that ordered dissolution during flow-through analysis removes high-Mg (primary) calcite first, followed by low-Mg (secondary) calcite, which provides a unique opportunity to extract initial calcification temperature (based on the Mg/Ca of the primary calcite), despite problems of shell heterogeneity and dissolution.

[30] These results are preliminary, and only represent regional (eastern tropical Pacific) findings from two species of planktonic foraminifera. Different species have different calcification schemes

that affect the relative abundances of primary and secondary calcite. In addition to Mg content, physical factors such as shape, morphology, and crystallinity may play a role in the observed order and patterns of dissolution [*Rushdi et al.*, 1998]. Further work is needed to deconvolve temperature and biomineralization effects on the Mg content of primary versus secondary calcite. Additional testing will also involve measuring core top Mg/Ca from several other depth transects in different ocean basins to see if the flow-through method consistently documents Mg heterogeneity in foraminiferal tests and yields accurate SST estimates despite exposure to water column and seafloor dissolution.

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