

## Evaluation of automated flow-through time-resolved analysis of foraminifera for Mg/Ca paleothermometry

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[1] The primary Mg/Ca ratio of foraminiferal shells is a potentially valuable paleoproxy for sea surface temperature (SST) reconstructions. However, the reliable extraction of this ratio from sedimentary calcite assumes that we can overcome artifacts related to foraminiferal ecology and partial dissolution, as well as contamination by secondary calcite and clay. The standard batch method for Mg/Ca analysis involves cracking, sonicating, and rinsing the tests to remove clay, followed by chemical cleaning, and finally acid-digestion and single-point measurement. This laborious procedure often results in substantial loss of sample (typically 30–60%). We find that even the earliest steps of this procedure can fractionate Mg from Ca, thus biasing the result toward a more variable and often anomalously low Mg/Ca ratio. Moreover, the more rigorous the cleaning, the more calcite is lost, and the more likely it becomes that any residual clay that has not been removed by physical cleaning will increase the ratio. These potentially significant sources of error can be overcome with a flow-through (FT) sequential leaching method that makes time- and labor-intensive pretreatments unnecessary. When combined with time-resolved analysis (FT-TRA) flow-through, performed with a gradually increasing and highly regulated acid strength, produces continuous records of Mg, Sr, Al, and Ca concentrations in the leachate sorted by dissolution susceptibility of the reacting material. Flow-through separates secondary calcite from less susceptible biogenic calcite and clay, and further resolves the biogenic component into primary and more resistant fractions. FT-TRA reliably separates secondary calcite (which is not representative of original life habitats) from the more resistant biogenic calcite (the desired signal) and clay (a contaminant of high Mg/Ca, which also contains Al), and further resolves the biogenic component into primary and more resistant fractions that may reflect habitat or other changes during ontogeny. We find that the most susceptible fraction of biogenic calcite in surface dwelling foraminifera gives the most accurate value for SST and therefore best represents primary calcite. Sequential dissolution curves can be used to correct the primary Mg/Ca ratio for clay, if necessary. However, the temporal separation of calcite from clay in FT-TRA is so complete that this correction is typically  $\leq 2\%$ , even in clay-rich sediments. Unlike hands-on batch methods, that are difficult to reproduce exactly, flow-through lends itself to automation, providing precise replication of treatment for every sample. Our automated flow-through system can process 22 samples, two system blanks, and 48 mixed standards in  $< 12$  hours of unattended operation. FT-TRA thus represents a faster, cheaper, and better way to determine Mg/Ca ratios in foraminiferal calcite. *INDEX TERMS*: 1045 Geochemistry: Low-temperature geochemistry; 1094 Geochemistry: Instruments and techniques; 4267 Oceanography: General: Paleooceanography; 4299 Oceanography: General: General or miscellaneous; *KEYWORDS*: flow-through, paleothermometry, Mg/Ca, paleoproxy, ICP-MS, paleoceanography

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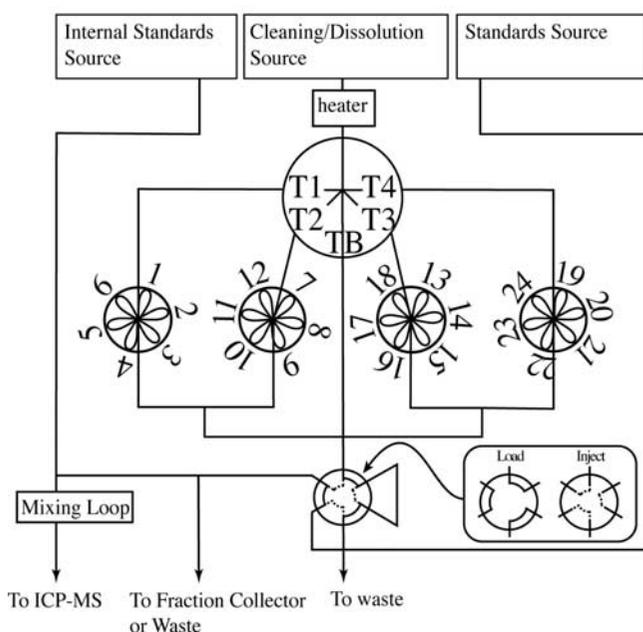
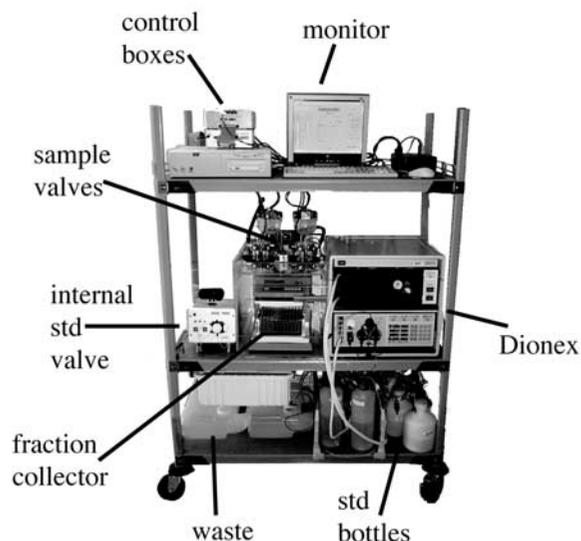
### 1. Introduction

[2] Rigorous cleaning of foraminiferal calcite began with the pioneering work of E. A. Boyle [Boyle, 1981; Boyle and Keigwin, 1985]. This batch procedure typically involves two types of cleaning: mechanical sorting and chemical leaching followed by removal of leachate with a pipette. Some type of preliminary sorting has always been seen to be critical for Mg

analysis because the Mg/Ca ratio in clay is  $\sim 1000$  times that of biogenic calcite. Sorting normally involves cracking and sonicating the shells and often includes rinsing with water, ethanol, methanol or other solvents. Chemical treatment involves removal of organic matter by reductive cleaning and etching to remove adsorbed contaminants. These steps were thoroughly examined by Barker *et al.* [2003], who recommend a rigorous procedure involving multiple sorting and leaching steps. After cleaning, the remaining sample is dissolved and the ratio measured by ICP-AES.

[3] Some time ago, our laboratory decided to develop the rare earth elements (REEs) as a new paleoproxy. It has been known for some time that batch cleaning is not effective for

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**Figure 1.** (top) FT-TRA leaching module. Control boxes for the valves, heater, and Dionex<sup>®</sup> are sitting on the left of the top shelf on the cpu of the PC that runs the LabView<sup>®</sup> control software. Left to right on the middle shelf are the valves for the internal standard, fraction collector with sample valve assemblies above, and Dionex chromatograph. Waste containers, standard and reagent bottles are on the bottom shelf. The unit is set up on a movable cart. (bottom) Schematic of the system.

the REEs as these elements tend to readsorb back onto calcite during cleaning. This problem prompted us to take a different approach. Instead of soaking shells in reagents, we decided to continuously leach and dissolve them in a flow-through (FT) stream as a way of minimizing readsorption [Haley and Klinkhammer, 2002].

[4] During the course of flow-through development we came to realize that the method was capable of resolving

the primary calcite signature, thus providing a way of minimizing the effects of ecology and dissolution on Mg/Ca ratios [Benway *et al.*, 2003]. However, there is another aspect of flow-through that we had not focused on until recently: the ability of the method to separate mineral phases. By adjusting the concentration gradients used in cleaning and dissolution, we have been able to optimize on-line separations to the point where contaminant phases have minimal influence on the determination of the primary Mg/Ca ratio. Flow-through thus provides a more reliable ratio with less effort by making pretreatment unnecessary.

[5] For this study, the FT leaching module was automated and coupled to a quadrupole ICP-MS instrument capable of rapid time-resolved analysis (TRA). The module-ICP combination makes up an analytical method that we call FT-TRA. This paper describes FT-TRA hardware and software, and explains phase separation with this method in detail. We also describe how data from the system can be used to address the major issues that have plagued the use of foraminiferal Mg/Ca as a paleoproxy, namely: ecology, contamination, and partial dissolution.

## 2. Methods

[6] The basic FT concept has been described elsewhere [Haley and Klinkhammer, 2002]. Since this first publication, the system (Figure 1) has been streamlined and automated by adding LabView<sup>®</sup> control of a series of valves that direct the sequential analysis of multiple samples and standards. The module responds to Gilson<sup>®</sup> control language which makes the unit digitally equivalent to an autosampler. This feature allows the system to be used with any ICP instrument capable of running TRA.

[7] The flow-through leaching module employs 24 disposable 13 mm diameter PTFE<sup>®</sup> syringe filter units with a 1.0  $\mu\text{m}$  pore size (Whatman<sup>®</sup> catalog no. 6784-1310) that serve as sample holders. Each filter unit is attached to one of four 6-place 24V solenoid-activated valves (NResearch Inc., part 225T092). A header valve selects among the four sample rosettes (Figure 1). A sample queue is set up in the LabView<sup>®</sup> operating program before each automated run. Cleaning reagents are selected by the chromatograph that runs its own program as a subroutine within the LabView<sup>®</sup> code.

[8] FT-TRA is a technique that can accommodate an endless number of methods. The Dionex<sup>®</sup> gradient pump makes it possible to control the dilution of reagents on-line, and it is a simple matter to add or modify reagents, standards, or leaching schemes as required. Figure 2 shows the cleaning and dissolution routine used in this study.

[9] Under fully automated control, it takes approximately 25 min to clean, dissolve and analyze each sample, including time to rinse and reset the system. A full array of 24 samples can be run in less than 12 hours, including loading. The procedure for Mg/Ca analysis of foraminiferal shells begins with 6 min of cleaning with 1N hydroxylamine at pH 9 (Figure 2). This treatment removes high-Mg calcite and coatings from the shells [Haley and Klinkhammer, 2002]. Next, a 5 min rinse with deionized water flushes the lines.

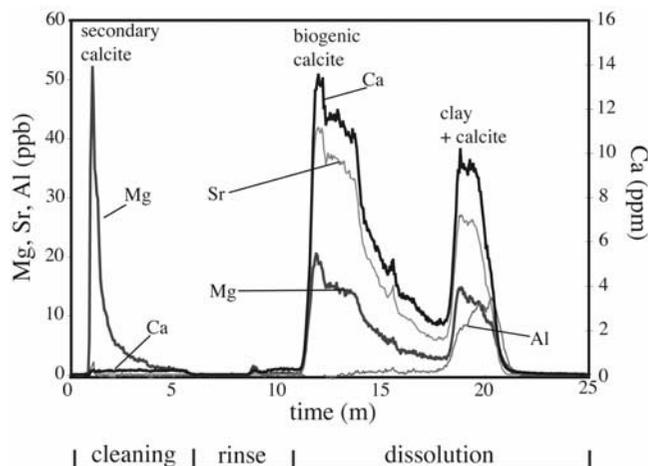
Finally, the sample is dissolved with nitric acid over the course of 14 min. The Dionex<sup>®</sup> gradient pump mixes 1.0 N HNO<sub>3</sub> with deionized water to produce the desired concentration, which can be changed at a controlled rate. The shape of this acid concentration gradient is key to attaining separation between different calcite and contaminant phases such as clay.

[10] The leaching module program is efficient and no instrument time is wasted. The ICP is continuously measuring either a sample or a standard. Before the effluent enters the mass spectrometer, it is mixed with a cocktail of internal standards covering the mass range of interest (in this case Be, Co, Y, and In). The internal standard count rates are steady ( $\pm 3\%$ ) during sample dissolution; i.e., there is no evidence for ion suppression or other nonlinear ionic interaction from Ca during the dissolution process [Haley and Klinkhammer, 2002]. Elemental counts from the samples and standards are normalized to mass-interpolated counts from the internal standards, and corrected for an average system blank developed from two blanks collected separately. System blanks for Ca are in the ppb range and in the ppt range for Mg, Sr, and Al. Blanks are reproducible and typically  $<1\%$  of analyte concentrations in the smallest samples. Mg, Sr, and Ca concentrations are each double-checked with two isotopes: <sup>43</sup>Ca—<sup>48</sup>Ca, <sup>25</sup>Mg—<sup>26</sup>Mg, <sup>86</sup>Sr—<sup>87</sup>Sr. These checks ensure that plasma artifacts such as double-charged <sup>86</sup>Sr on <sup>43</sup>Ca are insignificant. Duplicate concentrations from the isotopic pairs typically agree within analytical uncertainty and elemental abundances are routinely based on averages to yield a single concentration time series for each element. Normalized counts from the samples are used to calculate concentrations using standard curves that are also developed from blank corrected, normalized data. These standard curves are always linear. Seven standard reservoirs are used containing Ca up to 100 ppm with Mg and Sr in the proportions of biogenic calcite (up to 200 ppb).

[11] Two standards are incorporated into every sample run. A weighed portion of NIST 1c argillaceous limestone is dissolved and analyzed as an internal monitor. In addition, a powdered aliquot of a homogenous marble called the “Wiley standard” is used as a consistency standard from run to run. Ratios of the Wiley standard are reproducible within analytical uncertainty. For example, the average Mg/Ca ratio of the Wiley determined 12 times over the course of several days was  $4.39 \pm 0.26$  mmol/mol.

[12] Total flow out of the leaching module is about  $2.5 \text{ mL min}^{-1}$ , including the internal standard cocktail. The quadrupole ICP-MS takes about a third of this flow; the remainder is shunted to waste or to a fraction collector (Figure 1). Fractions are then available for other analyses using a different instrument. For example, if we want to measure the rare earth elements, the fractions would be taken to a high-resolution ICP-MS [Haley and Klinkhammer, 2002]. Fractions were not collected for this study.

[13] The quadrupole ICP-MS sweeps the sample stream about 6 times per second during TRA dwelling on masses in the analyte list, and producing a rich dataset. Analysis of a single sample results in about 1 Mb of raw text data over a period of  $\sim 25$  min. Taking standards and multiple samples

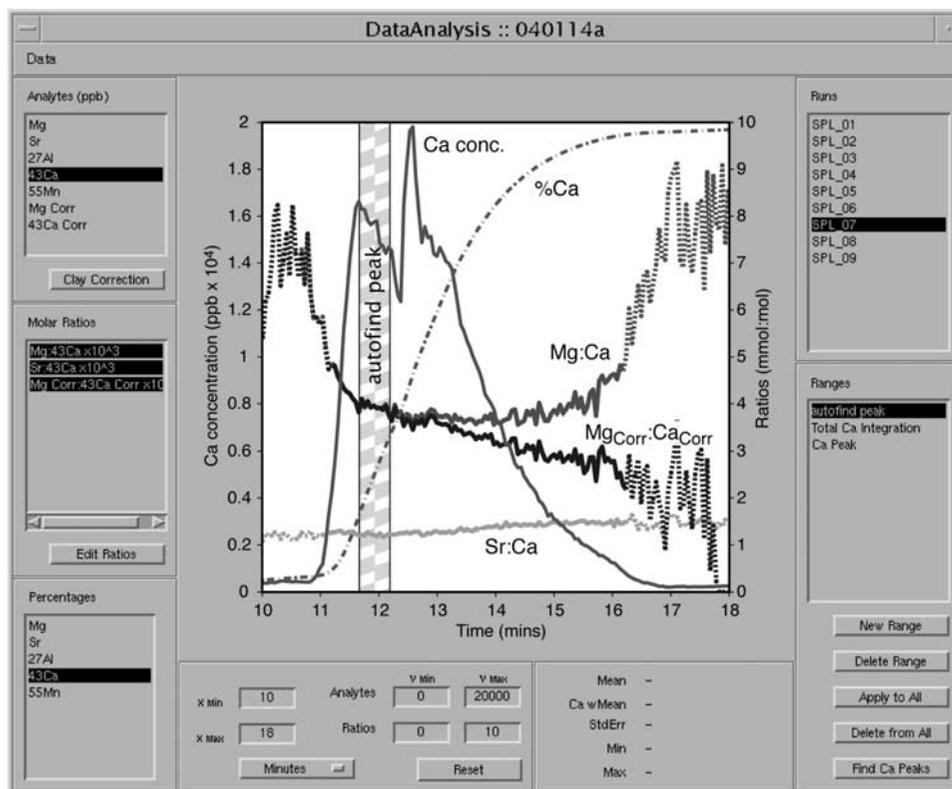


**Figure 2.** FT-TRA analysis of 12 shells of *G. sacculifer* contaminated with more than an average amount of clay. Leachate curves of Ca, Mg, Sr, and Al. Secondary calcite comes off in the cleaning step and clay is completely separated from the primary calcite peak. Al and elemental ratios are used to correct any overlap of clay on more resistant biogenic calcite.

into account, this process produces more data in the course of a 12-hour run than can be dealt with by standard spreadsheets such as Excel<sup>®</sup>. To overcome this problem we wrote a comprehensive program called BeaverDAMM (Data Analysis and Manipulation Module) based on the MATLAB<sup>®</sup> engine that reduces data from the module, normalizes data to an interpolated internal standard count rate, determines standard curves, calculates concentrations from these curves, corrects data for the system blank, and reports molar ratios and statistics.

[14] The BeaverDAMM code runs behind a GUI (graphical user interface) that allows the analyst to select envelopes of data from a time-resolved curve of ratios (Figure 3). This feature makes it possible to mathematically isolate biogenic calcite peaks from clay peaks during the analysis and makes it easy to compare the mass weighted average ratios of different fractions. For example, if we chose to calculate the calcium-weighted average from all the ratios in a dissolution curve developed from a cracked and cleaned sample, the resultant ratio would be equivalent to what would be obtained in a batch determination. In reality, it would rarely be advantageous to do this, as our intent with FT is to analyze and understand the spectrum of different elemental ratios present in the sample to obtain a better view of past oceanographic conditions [Benway et al., 2003]. Moreover, the ability of FT-TRA to isolate envelopes of data from the spectrum of Mg/Ca ratios making up the dissolution curve is key to dealing with important issues such as shell heterogeneity and partial dissolution.

[15] We use BeaverDAMM to isolate the “autofind peak” of the biogenic calcite dissolution curve that we believe represents the primary calcite of surface dwelling foraminifera. Planktonic species living deeper in the water column have more complex shell compositions that will require



**Figure 3.** “DataAnalysis” window in BeaverDAMM. The dashed parts of the curves indicate those sections where ratios are outside statistical acceptable limits (low Ca, Sr, or Mg). The software constructs the “autofind peak” by finding the first maximum in the derivative of %Ca and then selecting an envelope  $\pm 10\%$  around this point. There are typically  $\sim 200$  measurements within this envelope. As shown, BeaverDAMM reports the mean, Ca-weighted mean, standard error, minimum, and maximum of ratios in this range. Two families of Mg/Ca ratios are shown: uncorrected ratios (Mg:Ca) and those corrected for clay (Mg<sub>Corr</sub>:Ca<sub>Corr</sub>). The Ca-weighted mean of clay-corrected data in the “autofind peak” is the ratio reported in Tables 1 and 2, and represents the best estimate of the ratio in the primary calcite of surface dwelling foraminifera, as explained in the text.

further evaluation. BeaverDAMM constructs its “autofind peak” by locating the first maximum in the derivative of %Ca and then selecting an envelope of data  $\pm 10\%$  around this point (Figure 3). The “autofind peak” thus represents the initial fraction of biogenic calcite to dissolve, which is essentially the same definition used in our previous papers [Haley and Klinkhammer, 2002; Benway et al., 2003], except that the range is now selected by the software. BeaverDAMM reports the minimum, maximum, Ca-weighted average and standard error for ratios falling within this envelope. BeaverDAMM also allows the user to define other data envelopes using movable boundary lines, however, for this study we somewhat arbitrarily define the Ca-weighted average Mg/Ca ratio of the “autofind peak” as the primary ratio.

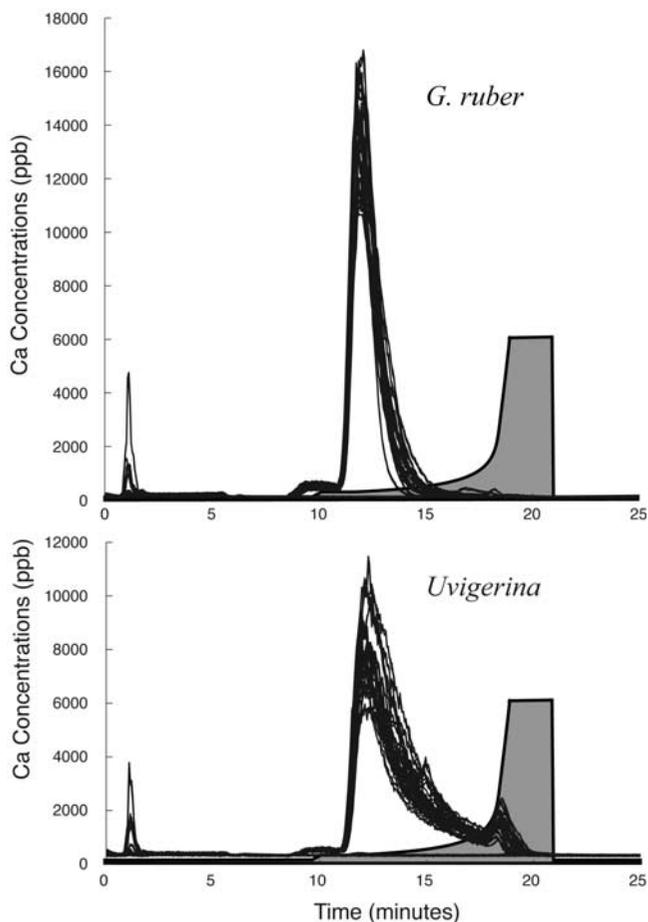
[16] The “autofind peak” occurs at exactly the same part of the dissolution curve in multiple analyses of the same shell type. This repeatability is one of the key features of FT-TRA. Because pumps control flow and acid concentration precisely, dissolution is reproducible (within a few seconds) resulting in reproducible Ca dissolution profiles for similar shells (Figure 4). While “autofind peaks” were used for this study, there may be other useful information in

the dissolution curve. One of the features of FT-TRA is the fact that the files are stored and can be reinterpreted.

[17] BeaverDAMM overlays Al dissolution curves on those for Ca, Mg, and Sr (Figure 2) produced during the same sequence. We use Al to estimate contributions from clay to the Mg/Ca ratio curve by making the reasonable assumption that all detectable Al comes from clay. BeaverDAMM gives us the choice of using empirically determined molar ratios for Mg/Al and Ca/Al in the clay phase or tabulated values (0.28 and 0.074 [Taylor and McLennan, 1985]). BeaverDAMM determines the empirical values for each sample by looking at ratios underneath the largest Al peak. Tabulated values are used if low levels of clay are present. We then calculate the clay contribution to Mg and Ca from the following equations:

$$\text{Mg}_{\text{corr}} = \{[\text{Mg}]_{\text{meas}}\} - \{[\text{Al}]_{\text{meas}} \times (\text{Mg}/\text{Al})_{\text{clay}}\} \quad (1)$$

$$\text{Ca}_{\text{corr}} = \{[\text{Ca}]_{\text{meas}}\} - \{[\text{Al}]_{\text{meas}} \times (\text{Ca}/\text{Al})_{\text{clay}}\} \quad (2)$$



**Figure 4.** Ca dissolution curves from one run of the FT-TRA analysis for samples of (top) planktic (*G. ruber*) and (bottom) benthic (*Uvigerina peregrina*) foraminifera (12 shells in each sample). The shaded curve is the concentration of HNO<sub>3</sub> that ramps up to 1.0 M. Several features are shown in Figure 4: Both planktics and benthics contain variable amounts of secondary calcite (the small Ca peak during cleaning, at ~1 min). The onset of biogenic calcite dissolution in the system (at ~11 min) is reproducible to a few seconds; the shapes of the dissolution profiles are reproducible and vary with species. Significant Ca is leached from clay only after the acid level is ramped up, and the *Uvigerina* shells contained more clay than the shells of *G. ruber*.

The result of equation (1) is multiplied by 1000 then divided by the result of equation (2) to obtain the clay corrected ratio in  $\text{mmol mol}^{-1}$ .

[18] BeaverDAMM uses this calculation to make a correction, as illustrated in Figure 3, for a sample that had more than an average amount of clay. Calcite and clay are so well separated by FT that Al is undetectable when the primary calcite peak comes off (Figure 2), resulting in a clay correction on the Ca-weighted Mg/Ca ratio that is typically  $\leq 2\%$  of the primary peak ratio (Table 1). This result can also be shown by calculation: The detection limit for Al is 200 ppt. Using this value and the Mg/Ca

molar ratio of clay (0.28), the maximum amount of Mg coming from clay when Al is undetectable is 2 nmol. Assuming Ca in the primary peak is 10 ppm this would mean that  $<0.01 \text{ mmol mol}^{-1}$  of the Mg/Ca ratio is supported by clay when Al is undetectable. As the shells dissolve and the biogenic Ca signal diminishes any clay present in the sample begins to be attacked as the acid strength ramps up (Figure 4). In a clay-rich sample, the signal eventually becomes dominated by clay in the latter stages of the leach, as illustrated in Figure 2. However, at this point most of the foram has dissolved and the ratio of primary calcite has been duly recorded.

[19] We are able to account for all the Mg, Ca, Sr and Al in the sample when we use the clay model. This is an important observation because it means that the Mg/Ca and Sr/Ca ratios during the FT dissolution procedure are a simple mixture of clay and biogenic calcite. While other phases are undoubtedly present, they are not significant for the ratios of interest.

### 3. Results

[20] FT-TRA produces leachate curves of elemental concentrations and ratios like those shown in Figure 3. The cleaning and rinsing steps are not shown in Figure 3, but they would be similar to that shown in Figure 2. As discussed above, the “autofind peak” shown in Figure 3 is our interpretation of what best represents primary biogenic calcite.

[21] When we first developed flow-through [Haley and Klinkhammer, 2002; Benway et al., 2003] we were analyzing foraminiferal shells that had been cracked, sonicated, and rinsed with ethanol as typically done to remove clays prior to chemical cleaning [Barker et al., 2003]. However, as we further developed the method, we realized that we were not always able to reproduce duplicate analyses within internal analytical precision ( $\pm 3\%$ ) using this procedure. We then undertook a series of tests in an attempt to isolate the source of this inconsistency. The results of one such experiment are shown in Figure 5. In this illustration, the rigor of cleaning increases from left to right. We found that cleaning with ethanol with no cracking removed calcite but not much clay (presumably because much of the clay was effectively locked inside the shells) and Ca-weighted average ratios in primary peak and total sample integrations both increased. Cracking and cleaning removed some of the clay, but also eroded the shell leading to erratic results, with higher ratios being obtained if there was even a speck of clay remaining. On the basis of these and similar results we decided to eliminate pretreatment altogether by developing a procedure that would separate calcite from clay on-line during the leaching process. To accomplish this we took a milder approach to cleaning and used weaker acid during dissolution. The acid concentration curve used for this study is shown in Figure 4 overlain on Ca leachate curves for multiple samples of *G. ruber* and *Uvigerina* run through the module.

[22] We evaluated separation and reproducibility characteristics of the new leaching procedure (Figure 2) by

**Table 1.** Reproducibility of Flow-Through Ratios in Untreated Samples<sup>a</sup>

Sample	Mg/Ca (Corrected)	$\Delta$ (Mg/Ca)	Sr/Ca (Corrected)
<i>ME0005A 38MC5<sup>b</sup></i>			
1	3.69 ± 0.05	-0.01	1.42 ± 0.02
2	3.91 ± 0.05	-0.05	1.44 ± 0.02
3	3.85 ± 0.05	-0.06	1.47 ± 0.01
4	3.72 ± 0.06	-0.02	1.46 ± 0.01
5	3.79 ± 0.05	-0.03	1.45 ± 0.01
Mean and 1 SD	3.79 ± 0.09 (2.4%)		1.45 ± 0.02 (1.4%)
<i>Leg 202, 1242A 1H5<sup>c</sup></i>			
1	3.85 ± 0.04	-0.01	1.42 ± 0.01
2	3.96 ± 0.04	-0.00	1.44 ± 0.02
3	3.85 ± 0.03	-0.01	1.49 ± 0.02
4	4.07 ± 0.04	-0.02	1.44 ± 0.01
5	3.92 ± 0.04	-0.10	1.45 ± 0.01
Mean and 1 SD	3.93 ± 0.09 (2.3%)		1.45 ± 0.03 (2.1%)
<i>Leg 202, 1242A 1H2<sup>d</sup></i>			
1	3.13 ± 0.03	-0.00	1.41 ± 0.01
2	3.14 ± 0.06	-0.03	1.35 ± 0.02
3	3.10 ± 0.05	-0.02	1.24 ± 0.02
4	3.25 ± 0.08	-0.12	1.30 ± 0.01
5	3.23 ± 0.06	-0.05	1.30 ± 0.01
Mean and 1 SD	3.17 ± 0.06 (1.9%)		1.32 ± 0.06 (4.6%)

<sup>a</sup>Samples consisted of 12 *G. ruber* shells (250–355  $\mu\text{m}$  fraction) placed in the leaching module uncracked and uncleaned. Ratios are Ca-weighted averages from approximately 200 ratios in the envelope of primary calcite selected by the BeaverDAMM software and shown as the autofind peak (Figure 3). Uncertainties on individual ratios are standard errors around the mean; uncertainties on the mean ratio among replicates are  $\pm 1\sigma$ . Clay corrections were applied to all ratios (see text);  $\Delta$  Mg/Ca is the difference between corrected and uncorrected ratios. Corrections for clay on Sr/Ca ratios are not listed but were  $<0.01$  mmol mol<sup>-1</sup> in every case.

<sup>b</sup>At 0–5 cm.

<sup>c</sup>At 12–14 cm.

<sup>d</sup>At 32–34 cm.

running duplicate samples of *G. ruber* from clay-rich cores taken in the eastern equatorial Pacific. These results are given in Table 1. The average standard deviation of the elemental ratios in replicate samples of foraminifera from this FT-TRA procedure is 0.08 mmol mol<sup>-1</sup> (2.2%) for Mg/Ca and for 0.04 (2.7%) for Sr/Ca. For comparison, the standard deviations of ratios found using batch analysis within laboratories average 0.17 for Mg/Ca, and 0.02 for Sr/Ca, and between laboratories are 0.31 for Mg/Ca, and 0.04 for Sr/Ca. [Rosenthal *et al.*, 2004]. This comparison suggests that at least some of the uncertainty associated with determinations of Mg/Ca by batch are problems associated with aggressive cleaning, which FT-TRA circumvents.

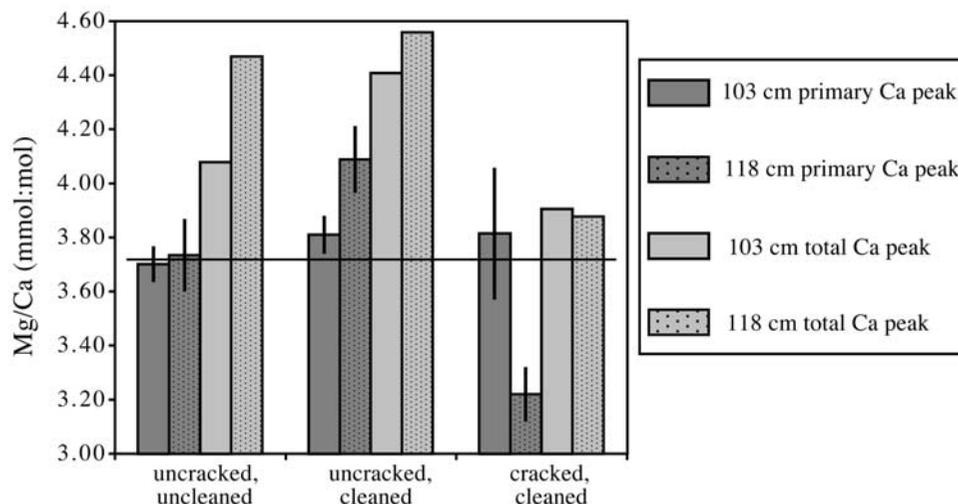
[23] In a second set of samples we evaluated accuracy and the ability of FT to “see through dissolution” by running core top samples of *G. tumida* and *G. sacculifer* from a series of carbonate rich cores taken as a depth transect on the Ontong Java Plateau (OJP) in the western equatorial Pacific. The same species collected in cores from the same transect had been used previously to illustrate dissolution trends as decreasing Cd/Ca, Sr/Ca [McCorkle *et al.*, 1995] and Mg/Ca, Sr/Ca ratios [Brown and Elderfield, 1996] with water depth. The OJP ratio data are summarized in Table 2 and displayed in Figure 6; SST results from the partial dissolution experiment are compared to water column temperature data in Figure 7. When we calculated SST from Mg/Ca, we avoided equations that contain a depth correction [Dekens *et al.*, 2002; Rosenthal and Lohmann,

2002] and instead chose the calibration developed by Anand *et al.* [2003] from sediment trap data, where Mg/Ca =  $0.38\text{Exp}(0.090T)$ .

## 4. Discussion

### 4.1. Advantages of Flow-Through

[24] The batch method for Mg/Ca involves an elaborate sorting and cleaning procedure followed by a single-point measurement [Barker *et al.*, 2003]. A significant amount of calcite is lost during the multistep batch cleaning process (30–60%), and there is typically no record of the Mg/Ca ratio(s) of this missing material. This approach contrasts sharply with the flow-through leaching procedure proposed here where an untreated sample is cleaned and dissolved over time while monitoring the Mg and Ca content of the leachate (Figure 3). Besides the obvious advantage of eliminating potential problems with fractionation resulting from loss of sample, FT-TRA of untreated shells produces thousands of Mg/Ca ratios for each sample sorted by calcite susceptibility. This data-rich analysis provides a wealth of information about shell heterogeneity related to the ecology of individual foraminiferal species. Statistical analysis of these ratios yields error bars on SST related to inherent heterogeneity of the shells, and not simply analytical uncertainty. As discussed in the following sections, the highly resolved view of elemental composition provided by FT-TRA is also a powerful tool for minimizing uncertainties from several



**Figure 5.** Replicate analyses of *G. sacculifer* under different pretreatment schemes of offline (batch) cleaning, followed by FT-TRA analysis. These data indicate that cracking and cleaning for clay as a pretreatment leads to variations in the Mg/Ca ratio that are outside the limits of analytical reproducibility ( $\pm 3\%$ ). The horizontal line indicates the true value for these shells determined by repeated measurements with the improved FT-TRA procedure (done later as a separate experiment). Two values are reported from each of two samples: the darker bars are the Ca-weighted average ratios under the “autofind peak” with standard error of the measurement (see Figure 3). The lighter bars are the Ca-weighted average ratios from under the entire Ca envelope (i.e., total integration). Because of clay influence, total integration yields higher Mg/Ca ratios than the “autofind” Ca peaks. Cleaning without cracking increases Mg/Ca because clay (probably packed inside the shells) is preserved at the expense of calcite, some of which is removed during batch cleaning. Cracking and cleaning does remove clay, and therefore reduces the Mg/Ca ratio from total Ca, but also erodes the shell, and leads to poorly reproducible and inaccurate results by preferentially eliminating relatively high Mg/Ca, or exaggerating the effects of small amounts of residual clay as shown by the high total Ca values.

other potential sources commonly associated with foraminiferal paleothermometry.

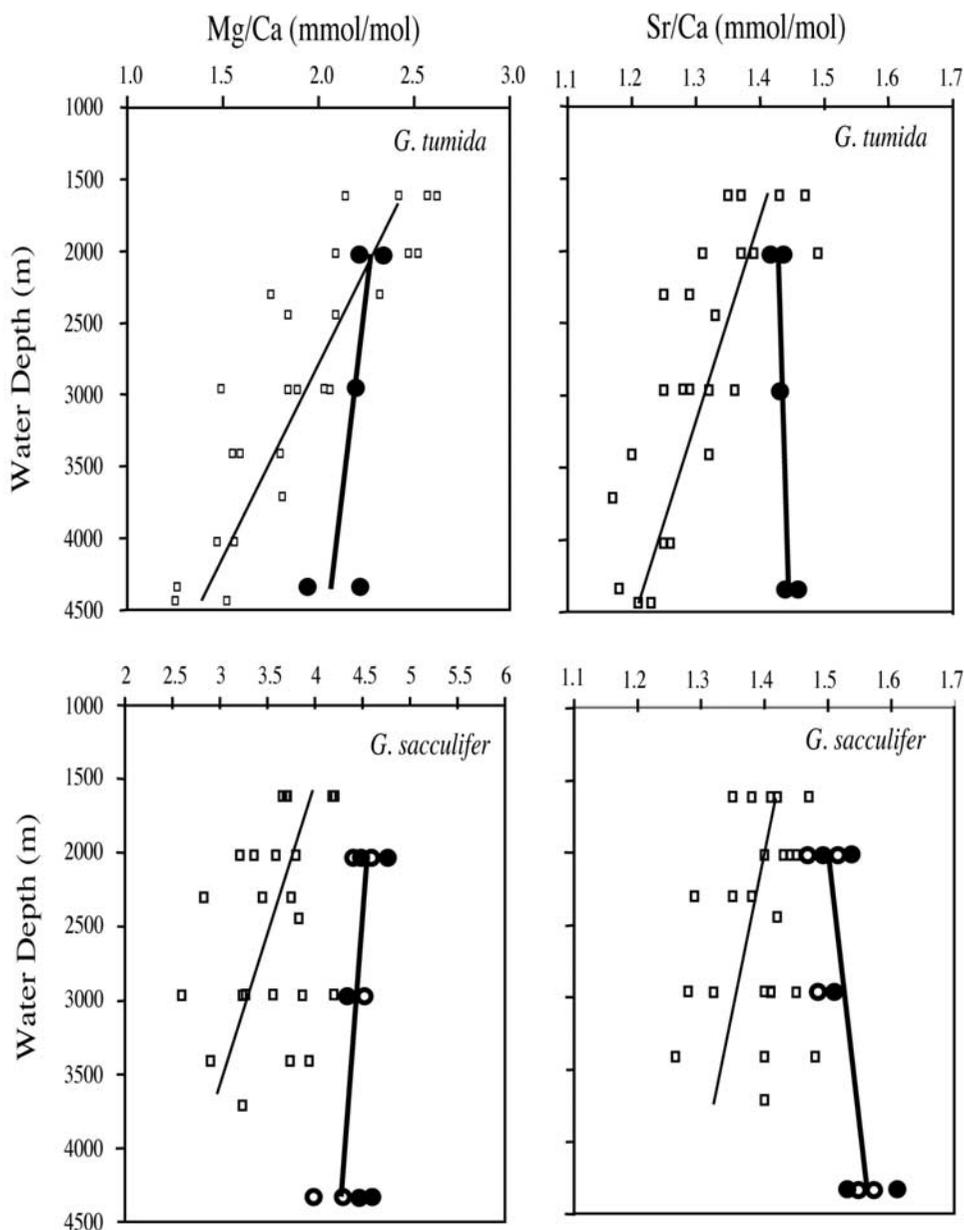
#### 4.2. Secondary Calcite

[25] As pointed out in a previous publication [Haley and Klinkhammer, 2002], a significant amount of Mg comes off at the beginning of the cleaning step. This early release of Mg and Ca is shown in Figure 2. Relative to the total shell, the phase released during cleaning contains a relatively small amount of Ca; at most a few percent in the samples we have analyzed to date. This highly susceptible phase is observed in tests of both benthic and planktic foraminifera, but is well separated from bulk shell in both cases (Figure 4). It is still unclear exactly what this phase represents: this will be determined as more types of samples are analyzed by FT-TRA (e.g., pristine samples from plankton tows and culture experiments). However, preliminary work suggests that this is secondary nonbiogenic calcite (authigenic or diagenetic). Two lines of evidence support this inference. Firstly, the fact that this material is more susceptible to dissolution than bulk shell is consistent with theoretical and laboratory studies of abiotically precipitated calcite [Mucci and Morse, 1984; Rushdi *et al.*, 1998; Davis *et al.*, 2000]. Secondly, the Mg/Ca molar ratio of this material is approximately  $50 \text{ mmol mol}^{-1}$ , which is in agreement with the experimental  $K_d$  of authigenic calcite determined

by Katz [1973] that would predict a ratio of  $20 \text{ mmol mol}^{-1}$  at  $25^\circ\text{C}$  [Tripathi *et al.*, 2003]. If this material is secondary calcite as we suggest, its relatively high Mg/Ca ratio would give it increasing importance as more and more of the sample becomes recrystallized. Nevertheless, the fact that this phase can be so cleanly isolated gives us hope that the FT-TRA method can improve data sets for older, partially recrystallized samples. The composition of this material may eventually have value in its own right both as an additional paleoproxy and as a tool for understanding recrystallization processes in the water column and on the sea floor.

#### 4.3. Clay Contamination

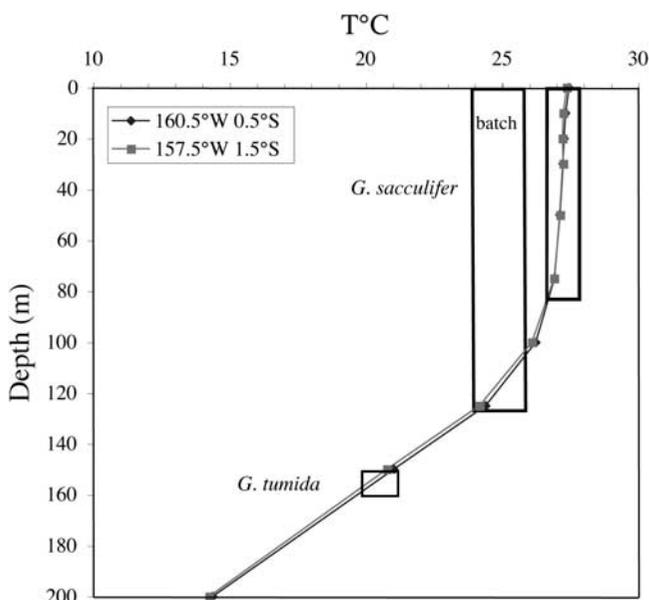
[26] As pointed out by Barker *et al.* [2003], the greatest potential problem related to recovering the primary calcite signature from sedimentary shells of foraminifera is clay contamination. This concern is for good reason as the Mg/Ca molar ratio of pelagic clay is  $1650 \text{ mmol mol}^{-1}$  [Taylor and McLennan, 1985], or nearly 3 orders of magnitude greater than that of foraminiferal calcite. This problem has precipitated much of the pretreatment normally associated with the batch Mg/Ca method. As illustrated in Figure 5, any attempt to remove clay also removes primary calcite, which is susceptible to physical disruptions and dissolution. It is clear that primary calcite is the first part of the shell to be lost in the ocean during partial dissolution,



**Figure 6.** Mg/Ca and Sr/Ca ratios of foraminifera collected from various depths on the Ontong-Java Plateau. Values were determined using batch analyses [Brown and Elderfield, 1996] (open squares and thin lines) and flow-through (FT-TRA, circles and thick lines; open symbols are from the 250–355  $\mu\text{m}$  fraction, solid circles from the 355–425  $\mu\text{m}$  fraction). FT-TRA ratios are for primary calcite determined without any batch pretreatments (Table 2). Vertical trend lines would indicate no impact on elemental ratios due to partial dissolution at the seafloor, which increases at greater water depth. As shown by the trend lines and scatter, FT-TRA results are less susceptible to partial dissolution on the seafloor or in the laboratory.

or in the laboratory during pretreatment. The effect of losing this material on the final Mg/Ca value depends on the species being analyzed. For example, partial dissolution during cleaning may prove to be a minor problem for *G. ruber*, a species that tends to construct relatively homogeneous shells, but may seriously degrade reproducibility and accuracy of Mg/Ca analyses in some other species such as *G. sacculifer*, which in our experience

precipitates relatively heterogeneous shells [Benway et al., 2003]. While regimented cleaning would eliminate some of the randomness generated by pretreatment [Rosenthal et al., 2004], regimentation will not recover accuracy (Figure 5). Only by retaining the entire sample and resolving its composition can we be sure that systematic bias caused by loss of primary calcite or contamination by clay has not affected the result.



**Figure 7.** Comparison of SST calculated from batch and FT-TRA results for *G. sacculifer* as shown in Figure 6; the width of the boxes represents  $1\sigma$  uncertainties. Data from *G. tumida* were taken from FT-TRA results. The temperature profile is from the OJP (World Ocean Atlas). FT-TRA ratios yield more precise and accurate estimates of SST.

[27] As shown in Figure 3, the primary biogenic calcite (the autofind peak) is well separated from clay (as represented by Al) with the FT-TRA procedure, as can be seen by comparing the corrected and uncorrected Mg/Ca ratios. However, there still can be significant overlap of clay with more resistant calcite in the latter part of the dissolution process. The degree of overlap fluctuates from sample to

sample depending on how much clay is present but also on the susceptibility of the shell material. For example, the group of benthics shown in Figure 4 contained more clay and were more resistant than the planktics shown in the same figure. Nevertheless, as shown in Figure 3, the clay correction produces useful Mg/Ca ratios for entire sample. The information gained from such curves will add to what we understand about calcification by different foraminiferal species.

#### 4.4. Foraminiferal Ecology

[28] Flow-through generates thousands of Mg/Ca ratios for each sample, but what ratio in the biogenic fraction is representative of primary calcite? Based on reproducibility of Mg/Ca and comparisons of data from surface-dwelling species such as *G. ruber* to surface-water temperatures, we infer that the Ca-weighted average ratio in the “autofind peak” (the first fraction to dissolve; Figure 3) in untreated samples is the best estimate of Mg/Ca related to SST. On the basis of quenching experiments, we reported previously that calcite fractions having different susceptibilities also have different Mg/Ca ratios that relate to different parts of the shell, and that the susceptibilities of these parts are consistent with what we observe in samples partially dissolved on the sea floor [Benway *et al.*, 2003]. We tentatively conclude that most surface-dwelling foraminifera produce calcite with the highest Mg/Ca in the earliest stages of growth and that lower Mg/Ca represents calcification deeper in the water column. This conclusion is consistent with our finding that the most susceptible fraction of *G. sacculifer* from the OJP gives an accurate estimate of SST (see the next section). While more work with other species needs to be done, this view is gaining support. For example, McKenna and Prell [2004] concluded recently that higher Mg/Ca ratios in deeper dwelling *G. truncatulinoides* (R) are related to primary calcite.

[29] In general, the Mg/Ca ratios of planktonic species are consistent with what we know about their ecology:

**Table 2.** Ontong Java Plateau Results<sup>a</sup>

Core	Water Depth, m	Fraction, $\mu\text{m}$	Mg/Ca, mmol/mol	Sr/Ca, mmol/mol
<i>G. tumida</i>				
BC37	2022	355–425	2.24	1.42
BC33	2024	355–425	2.35	1.43
BC22	2965	355–425	2.19	1.43
BC58	4329	355–425	1.86	1.46
BC66	4329	355–425	2.22	1.44
BC66	4329	250–355	2.22	1.37
Mean and 1 SD			$2.16 \pm 0.16$	$1.41 \pm 0.04$
<i>G. sacculifer</i>				
BC37	2022	250–355	4.43	1.51
BC37	2022	355–425	4.45	1.50
BC33	2024	250–355	4.57	1.48
BC33	2024	355–425	4.80	1.54
BC22	2965	250–355	4.48	1.49
BC22	2965	355–425	4.36	1.51
BC58	4329	250–355	4.34	1.46
BC58	4329	355–425	4.57	1.61
BC66	4329	250–355	3.79	1.57
BC66	4329	355–425	4.46	1.53
Mean and 1 SD			$4.38 \pm 0.29$	$1.52 \pm 0.05$

<sup>a</sup>OJP core designations, water depths, species, size fraction, Mg/Ca, and Sr/Ca ratios. All samples were 10–15 tests taken from core tops (0–5 cm) stored at Woods Hole Oceanographic Institution and collected during cruise MW91-9.

deeper-dwelling species have lower Mg/Ca ratios than surface dwellers. For example, we find that shells of *G. tumida* that are known to live in the thermocline have lower ratios than surface-dwelling *G. sacculifer* from the same samples, and temperature estimates produced using the same relationship between Mg/Ca and temperature predict plausible calcification depths (Figure 7, and discussed further in the next section). Moreover, since FT-TRA produces a continuous record of ratios, there is a potential to “play back” the calcification history of a shell as the percent calcite precipitated at various temperatures during its growth history. This idea is generally consistent with our observation that the shells of benthic foraminifera are considerably more homogeneous in Mg than any planktonic species (authors’ unpublished data, 2004), and is something that will be developed as more data become available.

[30] FT-TRA is the only available technique that sorts biogenic calcite by susceptibility to dissolution and allows elemental ratios to be computed for the primary biogenic calcite fraction while excluding other ratio populations in the bulk shell and contaminant phases. The shells of most species are at least partially heterogeneous with respect to Mg/Ca, and this heterogeneity will inevitably lead to errors in SST estimates based on bulk analyses. Moreover, the ability to recover the primary ratio becomes even more critical if the sample is partially dissolved, as discussed in the next section.

[31] Finally, FT-TRA sorts material based on its susceptibility to protons, which is a natural selection process occurring in the water column and on the sea floor. This capability sets our method apart from other microtechniques that provide information about shell heterogeneity on a small spatial scale, for example, laser ablation [Eggins *et al.*, 2003; Hathorne *et al.*, 2003]. We can thus hope to learn something more about the behavior of biogenic calcite postmortem by applying FT-TRA to a variety of foraminiferal species that we know exhibit a range of dissolution susceptibilities in the oceans [Berger, 1970; Lohmann, 1995]. In particular, FT-TRA provides precise quantitative data on the number of protons needed to dissolve shells. Such information could eventually lead to a dissolution index. This potential is another benefit of avoiding pretreatments such as crushing and sonicating shells, a process that could introduce artifacts into the susceptibility curve by creating an artificial size and weight distribution.

#### 4.5. Partial Dissolution

[32] The susceptibility of calcite to dissolution is influenced by the amount of Mg in the lattice, which is consistent with solubility studies and crystal lattice theory [Mucci and Morse, 1984; Rushdi *et al.*, 1998; Davis *et al.*, 2000]. The positive relationship between Mg/Ca and dissolution susceptibility is potentially a serious problem in using the ratio as a proxy for SST because dissolution can shift the calcium-weighted average ratio systematically lower, as has been shown in several previous studies [e.g., Brown and Elderfield, 1996; Hall and Chan, 2004]. This artifact has forced investigators to either choose cores from water depths shallower than the lysocline, or apply depth

correction factors [Dekens *et al.*, 2002; Rosenthal and Lohmann, 2002]. Placing restrictions on the depths of cores limits the potential of the Mg/Ca proxy; while corrections for depth add to the uncertainty of the SST estimate and are difficult or impossible to apply in the geologic record at times when the vertical profile of dissolution intensity may have been different from today. Moreover, dissolution problems can be compounded by batch procedures, which can further bias the measured ratio (Figure 5).

[33] Because the FT-TRA procedure captures the full spectrum of elemental ratios within an untreated sample, it has the potential of overcoming (or at least minimizing) artifacts related to dissolution. Of course, no method can measure the composition of material that is not present. This raises the important question: is there any primary biogenic calcite remaining in partially dissolved samples collected from the sea floor? One would guess there should be because primary calcite typically composes 60–80% of the shell [Benway *et al.*, 2003]. However, by addressing this question we will also determine the effectiveness of FT-TRA at overcoming partial dissolution.

[34] As illustrated in Figure 6, FT-TRA “autofind” data are more reproducible than batch analyses in the depth transect from OJP. Trends in Mg/Ca and Sr/Ca with water depth found with batch [Brown and Elderfield, 1996] virtually disappear with FT-TRA, indicating that the latter minimizes the effects of partial dissolution on the sea floor. Moreover, Mg/Ca and Sr/Ca ratios from the primary Ca peak plot at the high end of batch results, which is what we would expect if a significant amount of the more susceptible (higher Mg/Ca or Sr/Ca) calcite had been lost on the sea floor or during pretreatment in the laboratory during batch processing. Our finding that ratios taken from the beginning of the FT-TRA dissolution curve (primary peak ratios) for untreated samples are more or less constant with seafloor depth illustrates that the trend in the batch data is an artifact of measuring a Ca-weighted average. The FT-TRA results do not mean that the samples analyzed for this study were not partially dissolved on the sea floor; they certainly were, and this was obvious from the fragmentation and lacey appearance of the shells we observed during microscopic inspection and hand-picking of the samples from greater water depths. The degraded nature of these samples also would explain why their FT-TRA ratios were somewhat less reproducible (Table 2) than well-preserved samples (Table 1). Nevertheless, the results shown in Table 2 and Figure 6 demonstrate that FT-TRA was able to recover consistent ratios at all water depths, even under conditions of relatively severe dissolution, when only small amounts of primary material remained.

[35] The “autofind” FT-TRA ratios from partially dissolved samples are clearly more reproducible across a range of water depths (Figure 6), but do they produce accurate SST? To test the accuracy of FT-TRA ratios from the OJP we calculated SST from the data in Table 2 and the sediment-trap calibration of Anand *et al.* [2003]. The SST results are overlain on T-depth profiles in Figure 7. Summarizing these results, SST in the mixed layer over the OJP

is  $27.3 \pm 0.2^\circ\text{C}$  (World Ocean Atlas) compared to a SST of  $27.2 \pm 0.7^\circ\text{C}$  from FT-TRA. For comparison the published batch results averaged from all water depths at the OJP predict a SST of  $24.8 \pm 1.3^\circ\text{C}$  using the same equation, which would imply calcification at a depth  $>100\text{m}$ . The agreement in SST estimates from *G. sacculifer* Mg/Ca based on FT-TRA and true surface-water temperatures is extremely good. This result may be somewhat fortuitous since it is better than the calibration (although the calibration is reasonably well constrained at high SST such as this).

[36] The FT-TRA results for *G. tumida* yield a T of  $19.3 \pm 0.8^\circ\text{C}$  placing it in the thermocline at about 150 m (Figure 7). On the basis of  $\delta^{18}\text{O}$  analyses of bulk shells from Atlantic and Pacific core-top sediments, *G. tumida* is generally thought to calcify at depths averaging 100–250 m [Niebler *et al.*, 1999; Berger *et al.*, 1978]. A combination of plankton tow data and isotope data on living and seafloor specimens, suggest that *G. tumida* records hydrographic conditions at the base of the euphotic zone, which varies from 50–150 m but averages 100 m [Ravelo and Fairbanks, 1992; Faul *et al.*, 2000]. Living *G. tumida* (including some juvenile specimens) have been recovered in tropical Pacific plankton tows from the upper 100 m of the water column during active upwelling along the equator, and at depths of 50–100 m off the equator [Watkins *et al.*, 1996, 1998]. The  $\delta^{18}\text{O}$  of unencrusted and encrusted shells in Atlantic sediments suggested to Schweitzer and Lohmann [1991] that *G. tumida* calcifies its primary chambers within the upper 50 m of the water column, and adds a secondary crust late in its growth at depths of 50–100 m (applying a GEOSECS salinity profile, a relationship of seawater  $\delta^{18}\text{O}$  to salinity from the surface ocean, and a calcite equilibrium equation from molluscs). Our reanalysis based on atlas salinity profiles at the specific sites [Ocean Climate Laboratory, 1999], use of a depth-dependent relationship of seawater  $\delta^{18}\text{O}$  to salinity (G. A. Schmidt *et al.*, Global Seawater Oxygen-18 Database, available at <http://www.giss.nasa.gov/data/o18data>, 1999, and a modern calcite equilibrium  $\delta^{18}\text{O}$  equation from asymbiotic foraminifera [Bemis *et al.*, 1998] suggests that the calcite chambers in *G. tumida* studied by Schweitzer and Lohmann [1991] were formed at depths of 75–100 m, and crust was likely added at depths of 200–250 m. Thus the consensus view of calcification depths for *G. tumida* is that although some juvenile specimens can be found in surface waters, most primary calcification occurs near the base of the euphotic zone, and secondary calcification occurs much deeper, up to about 250 m. This conclusion is consistent with our results from the OJP.

[37] In summary, Mg/Ca ratios from FT-TRA of uncleaned shells are less scattered than from pretreated samples (Figure 6). We attribute this difference to random loss of primary calcite during batch pretreatment. SST results from the OJP (Figure 7) support our claims that FT-TRA makes it possible to isolate original Mg/Ca ratios from the primary calcite of surface-dwelling foraminifera, even after substantial partial dissolution on the sea floor, and yields more reproducible data and more accurate SST than conventional procedures.

## 5. Conclusions

[38] Flow-through time-resolved analysis (FT-TRA) isolates and resolves the elemental ratios of foraminiferal shells without sample pretreatment. Other phases that can affect the Mg/Ca ratio (such as secondary calcite and clay) are effectively separated from the primary material by mild cleaning and a highly controlled gradual increase in the strength of acid (and thus the rate of dissolution and leaching of the sample) during analysis. FT-TRA minimizes the effects of partial dissolution in the ocean or in the laboratory leading to more accurate estimates of SST than the commonly used batch method. We have automated the FT-TRA procedure, which has improved reproducibility of methods and the resulting data. Because no pretreatment or hands-on chemical manipulations are required, FT-TRA measurements are faster and less expensive to produce making the method advantageous for high-resolution down-core applications as needed for paleoceanographic reconstructions. Moreover, FT-TRA yields uncertainties on SST propagated from shell heterogeneity and not simply from analytical measurement. In summary, FT-TRA improves the precision of elemental measurements of foraminiferal shells, and expands the applicability of Mg/Ca paleothermometry to cores from deeper sites, species that make heterogeneous shells, and samples that have undergone partial recrystallization.

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