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Development of a flow-through system for cleaning and dissolving foraminiferal tests

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Abstract

A novel flow-through method for cleaning and dissolving foraminiferal shells is presented. Using automated chromatographic equipment, the system chemically removes contaminant phases from the shells. The cleaned calcite is then dissolved in a stream of weak acid for minor and trace element analyses. The system operates at elevated temperature (80 °C) and pressures (850–900 psi) and is extremely reproducible. This method has several advantages compared to traditional batch method cleaning done in centrifuge vials. The most important of these is that nothing is lost from the flow-through system, permitting complete monitoring of and greater insight into the effects of cleaning and dissolution. Development of this method revealed that it is necessary to remove two contaminant phases from the shells: an oxide coating phase that is rich in Mn, Cd, and Mg, and a refractory phase that is rich in Ba and the rare earth elements (REEs). This cleaning is accomplished through the use of basic hydroxylamine and basic diethylene triamine pentaacetic acid (DTPA) solutions, respectively. Time-resolved analysis (TRA) of shell dissolution demonstrates that *Orbulina* shells are composed of high-Sr and low-Sr calcite types. Other minor (e.g., Mg) and trace (e.g., Cd, REEs, Ba) elements show the same distribution during dissolution as Sr. In *Orbulina* shells, the high-Sr (high-Mg) calcite always dissolves first, similar to observations of natural dissolution in the ocean. Consequently, this flow-through system may provide a simple solution to dissolution problems in proxy work. Further, since flow-through can provide several measurements of elemental composition for each calcite type, the method allows for true statistical evaluation of homogeneity during growth of the shell. Most significantly, this flow-through method fully cleans calcite, and provides information about the calcite and contaminant phases and thus should prove to be valuable in advancing geochemical proxies as tools for paleoceanographic investigations.

Keywords: Foraminifera; Calcite; Paleoproxy; ICP-MS; Mg/Ca; Rare earth elements

1. Introduction

The use of geochemical proxies as tools for investigating paleoceanographic and paleoclimatic changes is increasing. Fundamental to this area of research is the concept that minor and trace element concentrations recorded in foraminiferal tests reflect the contemporary seawater chemistry. These elemental concentrations, normalized to calcium, can be measured in down-core samples and used to interpret changes in the ocean and climate systems over time. A few examples are Cd/Ca as a proxy for phosphate

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(e.g., Hester and Boyle, 1982; Boyle and Keigwin, 1987; Boyle, 1988; Delaney, 1990; Frew and Hunter, 1992; De Baar et al., 1994; Rosenthal et al., 1997; Martin and Lea, 1998; Elderfield and Rickaby, 2000); Mg/Ca as a proxy for temperature (Nurnberg et al., 1996; Hastings et al., 1998; Toyufuku et al., 2000; Elderfield and Ganssen, 2000; Lear et al., 2000); Ba/Ca as a proxy of silica and alkalinity (Lea and Boyle, 1993; Lea, 1993); V/Ca as a proxy of redox conditions of the surface sediments (Hastings et al., 1996); and U/Ca as a proxy of oceanic uranium or carbonate concentration (Russell et al., 1994; A. Russell, personal communication).

A major hindrance to the use of these proxies is that the foraminiferal calcite is prone to contamination by phases added post-mortem (Boyle, 1981). These processes can alter the original element/calcite ratio of the calcite, which in turn, can render the ratio measured inaccurate. Therefore, potential contaminants must be cleaned from the calcite.

Traditionally, foraminifera have been cleaned in polyethylene centrifuge vials as a "batch" method (Boyle, 1981; Boyle and Keigwin, 1985; Hastings et al., 1996). This method basically involves soaking the shells in reagents then siphoning the chemical cleaning reagents off during each step of cleaning. In the final step, the foraminifera are dissolved through the addition of acid to the vial.

Although this has been the only established method for cleaning foraminifera, the batch cleaning method has significant drawbacks. The process is time- and labor-intensive, complicated by the fact that the final cleanliness is limited by the analyst's experience. Also, the foraminifera are dissolved in only one step, thereby disallowing the opportunity for multiple measurements of a single sample. Given these limitations, some improvements to batch cleaning seemed warranted. However, the major impetus for developing this method was the notion that REEs tend to readsorb, and, although batch cleaning removes the contaminant phase initially, the REEs would readsorb onto the remaining "cleaned" calcite (Sholkovitz, 1989). As a result, the final REE/Ca ratios obtained by batch cleaning do not necessarily reflect lattice-bound calcite.

In order to overcome the problem of REE readsorption and other problems associated with batch cleaning, a novel "flow-through" cleaning method has been developed. This method makes use of automated chromatographic techniques, and the system described is readily built from available chromatographic components. In overview, the system pumps a continuous flow of cleaning reagents (eluates) over the sample, after which, weak acid is applied, dissolving the sample for measurement. The benefits of this method are reproducibility, complete enclosure (reducing potential for blanks), controlled dissolution with time, and the potential for continuous observation during cleaning and dissolution of the sample. Further, the system cannot approach equilibrium, as is possible in batch methods, but remains in steady state. Therefore, sample size and degree of contamination are not an issue in this method, as it may be in the batch method. Finally, because the flow is continuous, any contaminant REEs are removed from the sample before they can readsorb, thus eliminating this problem.

The primary goal of this paper is to present a novel method for cleaning foraminiferal calcite. However, because the flow-through method is the first to establish the opportunity for continuous analyses, not only the final dissolution but also of every cleaning stage, a few key observations are significant. One key finding is that REEs have proven to be highly concentrated in the refractory contaminant phases, rather than in the coating phases as previously thought (Palmer, 1985; Palmer and Elderfield, 1986). Another key finding is that there is chemically more than one type of calcite in cleaned samples. Although this has been observed previously (e.g., Bender et al., 1975; McCorkle et al., 1995; Brown and Elderfield, 1996), the flow-through method presented here offers the potential for greater insight into this feature of foraminiferal calcite, and may, in the future, readily solve the dissolution problems associated with Mg/Ca paleotemperature estimates (Lohmann, 1995; McCorkle et al., 1995).

2. The method

Development of the method described in this paper requires a large number of foraminiferal shells from the same core sample in order to be able to compare results between stages of development. For this reason, a core was chosen that had very abundant, large, and well-preserved foraminifera. All the foraminiferal data

presented here are, unless otherwise specified, ~ 11.5 mg samples of *Orbulina* from the Caribbean Core TT9108-1GC (11°39.83N, 79°35.52W, 2540 m water depth; see Hastings et al., 1998). The samples herein are from a core depth of 185–190 cm ("uncorrected depth", ~ 39.4 ka age). A deeper core sample was chosen in order to build confidence that contaminant phases would have the chance to precipitate. The large sample size was chosen for two reasons: first, the nature of contaminant phases would be easier to ascertain, and second, the signal-to-noise ratio would be higher with larger samples, especially for measuring REEs on the quadrupole ICP-MS.

2.1. System description

The basic concept for flow-through cleaning is simply to run the cleaning reagents over the sample as is done in chromatography. Similar to chromatography, flow-through cleaning would be possible by using a gravity column and by manually adding reagent. However, more control of the physical conditions and better reproducibility are gained using automated chromatographic equipment. The system described herein was assembled mainly using Dionex chromatographic equipment, which is readily available.

Although the idea of flow-through cleaning is straightforward, it has been found to require modifications for practical reasons. As a result, the plumbing of the system is slightly more complex than a single line, as is implied above. A schematic of the system is shown in Fig. 1, and is described in terms of a flow passing through five components, starting with the eluant reservoirs and moving downstream.

The cleaning reagents (eluants E1–E4) are pumped from individual reservoirs by an advanced gradient pump (AGP) at constant flow rates. Together with the proportioning valve (PV), the Dionex AGP module can be programmed to control the composition, flow rate, and as a corollary, the pressure of the eluate that flows through the system. Programming these parameters is straightforward and can be readily adjusted as needed. Importantly, once a program has been proven, the system will repeat it accurately and consistently. This is an important feature of the method because it allows for very controlled dissolution, as discussed later. The program that has been developed is listed in Table 1. The pressure of the eluate, measured at the AGP, is between 850 and 900 psi. This pressure is expected to be slightly less at the sample because the system is open-ended, and some pressure will be lost.

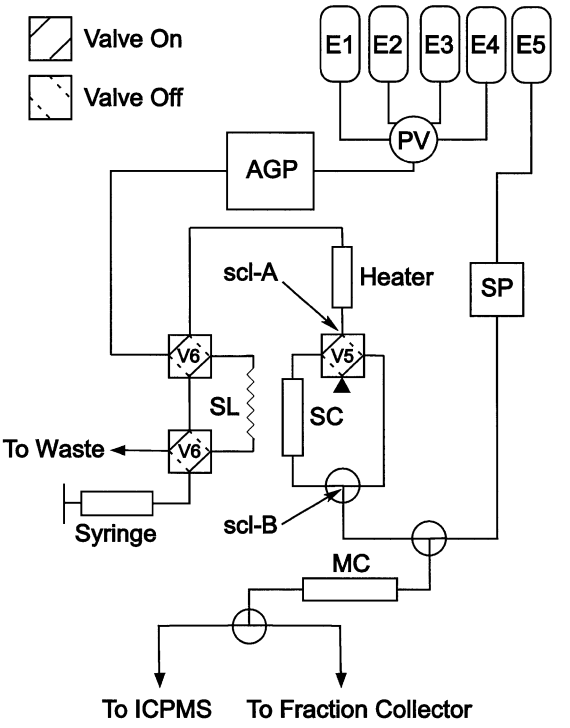

Fig. 1. Schematic of the system. Flow generally follows from top to bottom of the diagram. Eluants: E1: 0.5 M hydroxylamine (pH > 9), HYDRX; E2: 1 mM diethylene triamine pentaacetic acid (pH > 9), DTPA; E3: 0.5 M HNO_3, W.A.; E4: deionized water, DIW; E5: 2 M HNO_3, spiked with Be, In, Re; PV: proportioning valve; AGP: advanced gradient pump; SL: standard loop; SC: sample column; scl-A–B: sample column loop; MC: mixing column; SP: sample pump.

The eluate then passes through a heater set at 80 °C, as this has been shown to be the optimal temperature for cleaning (Palmer, 1985). Multiple measurements over 15 min duration demonstrate that the eluate temperature is constantly within 2° of 80 °C. This signifies that the eluate has reached equilibrium temperature and therefore will not vary during or between cleaning runs. The warmed, high-pressure eluant then flows into the sample column (SC). After passing over the foraminiferal sample, the resulting eluate continues to flow downstream. Thus, the sample is exposed to a constant flow of reagent.

Table 1
Timed sequence of events programmed into the Dionex AGP (see text for details on the sequence of events)

AGP program for flow-through cleaning and dissolution of foraminiferal tests								
E1: 0.5 M hydroxylamine (pH > 9); E2: 1 mM DTPA (pH > 9); E3: 0.5 M nitric acid; E4: deionized water								
T (min)	%E1	%E2	%E3	%E4	V5	V6	Flow rate (ml/min)	Event
0.0	100	0	0	0	0	0	4.0	Oxide coating phase removal
6.0	100	0	0	0	0	0	4.0	
6.1	0	100	0	0	0	0	4.0	Refractory phase removal
12.0	0	100	0	0	0	0	4.0	
12.1	0	0	100	0	1	0	4.0	System rinse
15.0	0	0	100	0	1	0	4.0	
15.1	0	0	0	100	1	0	4.0	
17.5	0	0	0	100	0	0	4.0	Sample rinse
20.0	0	0	0	100	0	0	4.0	
20.1	0	0	10	90	0	0	4.0	Sample dissolution
30.0	0	0	10	90	0	0	4.0	
30.1	0	0	0	100	0	0	4.0	Final DIW rinse, stop EXP

Next, the eluate passes from the sample column into a mixing tee, where the eluate mixes with a flow of 2 M HNO_3 that has been spiked with beryllium, indium, and rhenium. This step serves two purposes: first, the high pH eluate is acidified, preventing adsorption of elements to the walls of the system; and second, the Be, In, and Re are used as internal standards (Falkner et al., 1994) during continuous analyses by the ICP-MS (for details, see Table 2). The spiked acid solution (eluant E5) is pumped into the tee from a separate reservoir via a sample pump (SP) set to flow at 2 ml/min. Complete mixing is assured through use of a braided mixing line (MC), and the pH level of the eluate after acidification is always found to be less than 2.

After acidification and addition of internal standards, the eluate is split, using another tee. This is done to allow real-time continuous analyses by the ICP-MS, while still collecting discrete samples with a fraction collector for post-run measurements. Using different tubing sizes on each downstream arm of the tee, the eluate flow rates are set at 4 ml/min to the fraction collector and 2 ml/min to the ICP-MS. The fraction collector is set to collect 2.8-ml samples every 42 s.

The basic description of the system mechanics presented above are made slightly more complex through addition of valves. Valves 5 (V5) and 6 (V6) each have important, but different, purposes in this system. V5 is used in every run, as its purpose is to allow the system to be rinsed. As mentioned previously, the high pH cleaning reagents tend to allow adsorption of elements onto the walls of the system, resulting in a blank problem which develops over time. To overcome this, a rinsing step has been added to the method. With V5 in the OFF position, the sample

Table 2
ICP-MS characteristics

Instrument	VG Plasma Quad PQ2 + Quadrupole ICP-MS	VG Excell Quadrupole ICP-MS
Sample and skimmer cones	Nickel	Nickel
Sample flow rate	0.6 ml min^{-1}	0.6 ml min^{-1}
Argon flow rates		
Plasma gas	13.0 ml min^{-1}	13.0 ml min^{-1}
Auxiliary	0.80 ml min^{-1}	0.77 ml min^{-1}
Nebulization	0.80 ml min^{-1}	1.00 ml min^{-1}
RF Power	1350 W	1360 W
Data acquisition	Peak hopping	Peak hopping
Dwell time	10 ms	10 ms
Sweeps per reading	120	120
Channels per mass	3	3
Replicates per sample	3	3
Time Resolved Analysis (TRA)		
Dwell time	N/A	100 ms/mass
Time per sweep	N/A	7.2 s
Cooling temperatures	Interface 15 °C Spray chamber 5 °C	Interface 15 °C Spray chamber 3 °C

Typical instrument settings, operating conditions. Two instruments were used during the development of this method, as listed above.

column loop (scl-A to -B) is isolated from the flow of eluate. In this position, strong acid is flushed through the system and it rinses the whole system except for the sample column loop. Valve 5 then switches to the ON position, and deionized water (DIW) is pumped through the sample column loop. Acid cannot be used in this rinsing, as the foraminifera in the sample column would dissolve; the DIW is sufficient as a rinsing agent. Both valves automatically switch position as part of the program (Table 1). V6 is used only when continuous analyses by the ICP-MS are desired, as it simply allows for injection of standard solutions into the system to generate standard curves (Falkner et al., 1994).

2.2. System operation

Hand-picked foraminiferal shells of a single species are cleaned in four basic stages. In order, these are: (1) physically cleaning the sample (done externally to the system described); (2) chemically cleaning the sample; (3) rinsing the sample and system; and (4) dissolving the sample for elemental analyses of the cleaned foraminiferal calcite.

The first step in cleaning shells for flow-through or batch method is the removal of clays and other adhering detritus. Thus far, the only readily apparent method for accomplishing this is by physically cracking open the shells and sonicating off the clays. As a consequence, this stage remains time consuming. The flow-through method does, however, due to its predilection for automation, greatly reduce the man-hours spent chemically cleaning samples.

Large (>350 μm) *Orbulina* shells were chosen for development of this flow-through cleaning method because of their size and ease of picking. The shells are cracked open by being "milled" through a 125-μm sieve and collected in a 63-μm sieve. The fragments are then sonicated for 40 min in both deionized water (DIW) and ethanol, with DIW rinses following both initial "milling" and both sonication steps. After this, the foraminiferal shell fragments are checked visually under a microscope to verify that sonication and rinsing have removed the adhering clays and detritus and that the samples are completely fragmented. The sample is then dried at 50 °C in an oven and reweighed. This physical cleaning results in ~ 30–40% weight loss from the original foraminiferal sample. These fragments are then loaded by pouring them directly into a sample column (4-mm polypropylene syringe filter, with 1.0 μm pore sized PTFE filter material (Whatman; Cat. No. 6784-0410)). Once loaded, the sample can be cleaned and dissolved without ever being removed from the sample column.

Once the sample is in line with the system, three programmed stages are set into operation: (1) chemically cleaning the sample; (2) rinsing the system and the sample; and (3) dissolving the cleaned sample for analyses.

It is necessary to chemically clean the sample in order to remove contaminant phases that cannot be removed through physical cleaning. A classic example of a contaminant phase is the oxide coating, postdepositionally precipitated onto the foraminiferal shell. These coatings are known to be rich in certain metals such as manganese and cadmium (Boyle, 1981; Boyle and Keigwin, 1985,1987). As will be discussed in detail later, it is also important to chemically clean for another "refractory" phase, which is rich in REEs.

The first step of the chemical cleaning procedure entails removal of the oxide coatings. This is accomplished in a solution of 0.5 M hydroxylamine, brought up to pH 9 with ammonium hydroxide (eluant E1; see Table 3 for details). In batch methods, coatings are removed by soaking the sample in basic solutions of hydrazine (Boyle, 1981). However, by using hydroxylamine instead of hydrazine, it is necessary to use fairly concentrated hydroxylamine, because it is less effective at higher pHs (E. Boyle, personal communication). As described later, this new method allows the cleaning process to be monitored, as shown in Fig. 2. As cleaning proceeds, manganese concentrations decrease exponentially in the eluate (Fig. 2) as predicted, if the sample is being cleaned of oxide coatings.

The next step in the chemical cleaning procedure is removal of the "refractory" phases. This is accomplished in a solution of 1 mM diethylene triamine pentaacetic acid (DTPA), brought up to pH 9 with ammonium hydroxide (eluant E2; see Table 3 for details). Lea and Boyle (1993) first used this reagent to clean foraminiferal calcite with respect to barium contamination. However, the flow-through work accomplished here has found that the REEs, which act in a manner similar to barium in many ways, are also enriched in this "refractory" phase.

Table 3
Reagent characteristics

Reagent	Preparation	pH	Purity[a]	Matrix effects[b] (%)	Blanks/detection limits[c]				
					Ca (ppm)	Sr (ppb)	Mn (ppb)	Ba (ppb)	La (ppt)
HYDRX 0.5 M Hydroxylamine (Mallinckrodt (5258))	34.76 g NH_4OH·HCl		Reagent grade 18.2 MΩ Ltd	80–90	1.36/ 0.053	1.41/ 0.35	1.38/ 0.67	3.78/ 4.21	9.01/ 3.45
	+800.0 ml Milli-Q water	~ 4							
	+200.0 ml 4 N NH_4OH	> 9							
DTPA[d] 1 mM diethylene Triamine Pentaacetic acid (Aldrich (D9,390-2))	0.39 g DTPA		97% 18.2 MΩ Ltd	90–100	1.33/ 0.091	4.90/ 2.07	0.91/ 12.15	79.63/ 128.53	70.70/ 91.01
	+993.0 ml Milli-Q water	~ 4							
	+7.0 ml 4 N NH_4O_4	> 9							
W.A. 0.5 M Nitric acid	967.7 ml Milli-Q water		18.2 MΩ	95–100	1.295/ 0.016	0.75/ 0.05	0.10/ 0.04	1.68/ 0.70	8.44/ 2.75
	+32.3 ml 15.5 N Qd HNO_3	< 3	Qd						
Neutralization/Spike solution[e] In, Re, Be standard solution in a 2M nitric acid solution.	1.6 ml 10 ppm In				(Included in blanks/detection limits of reagents listed above)				
	1.6 ml 10 ppm Re								
	3.2 ml 10 ppm Be								
	+1607.7 ml Milli-Q water								
	+385.9 ml 15.5 N Qd HNO_3	< 3	Qd						

[a] Qd = Quartz distilled; Ltd = Low temperature distilled (i.e., the ammonium hydroxide solution (NH_4OH) is cleaned by low temperature distillation in a sealed container using reagent grade ammonium hydroxide and Milli-Q water). The nitric acid is quartz distilled (Qd) from reagent grade nitric acid.

[b] Matrix effects represents the relative sensitivity of the ICP-MS resulting from running the reagent. This is a qualitative measure given by the percent amount of indium (in CPS) compared to the weak acid (W.A.) solution. The weak acid solution (0.5 M HNO_3) is nearly optimal running solution for the ICP-MS.

[c] X/Y; where X = Average blank of > 320 individual measurements of each solution, Y = detection limit of element in the solution (= 3 × standard deviation of > 320 measurements).

[d] Due to the slow dissolution of the DTPA powder in water, this solution is made on a warm hot plate.

[e] Internal standard solutions are diluted from SPECPURE ICP standard solutions.

The removal of the "refractory" phase is difficult to represent because the elemental concentrations in the eluate are generally below given detection limits, due to significant matrix problems associated with measuring a solution of DTPA in the mass spectrometer. The best evidence that an important contaminant phase is removed is seen in the difference in the REE/Ca ratios of the dissolved foraminifera of samples that have and have not been cleaned for the "refractory" phase (Fig. 2). This will be discussed in detail in Section 4. Otherwise, the best direct observation that removal of a contaminant phase is occurring is in the fractions collected during the start of the DTPA step and the start of the rinsing steps (Fig. 3). In both cases, a spike of Ba is observed, indicating removal of a Ba-rich phase. Also, the time-resolved analysis (TRA) data shows that barium concentrations are very high during this stage of cleaning, as would be expected for removal of such a phase. As shown, there is not a simple exponential decrease in the Ba/Ca curve like the Mn/Ca curve described above. This is because barium (and the REEs) most readily adsorbs onto surfaces in high pH solutions. Therefore, as the refractory phase is removed, these metals adsorb onto the system walls. This mandates the need for a rinsing stage in the system operation.

While high pH solutions reduce dissolution of the calcitic foraminifera sample during cleaning, they also promote adsorption of certain elements onto surfaces. The method overcomes contamination by adsorbed

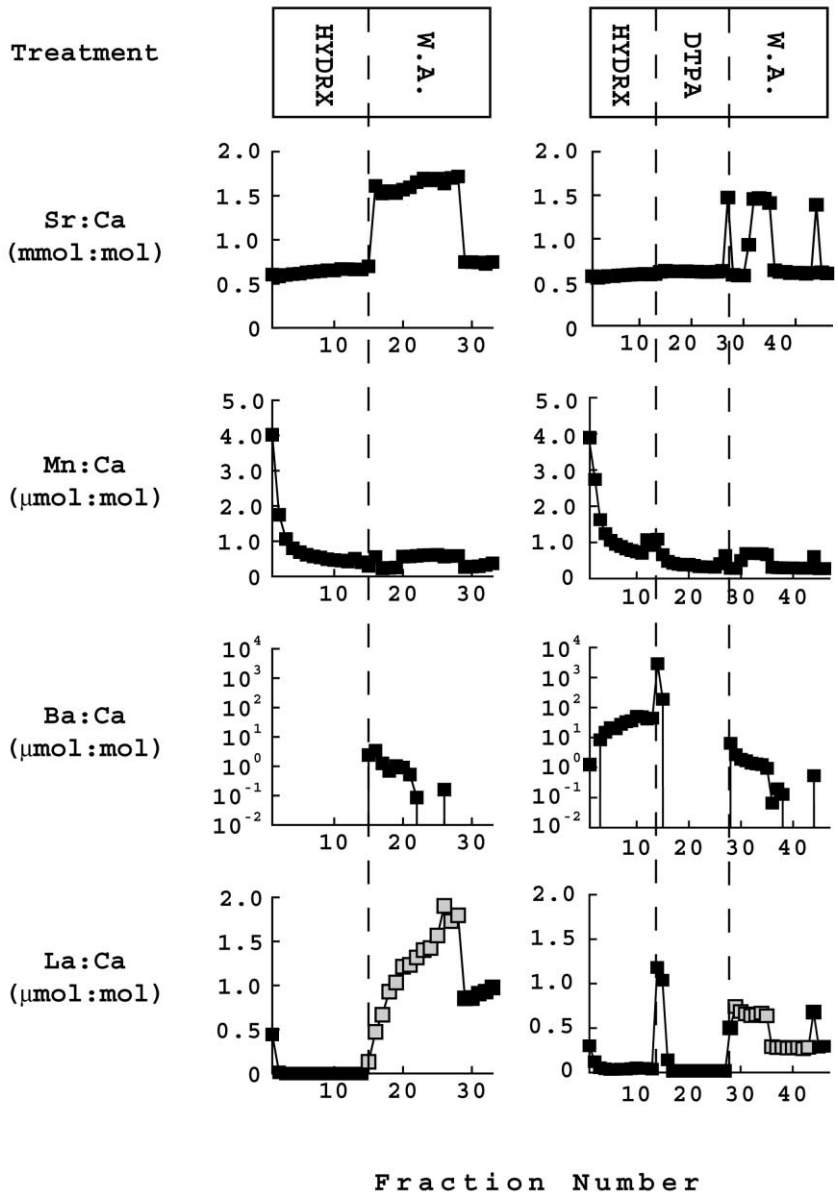

Fig. 2. Comparison of element/calcium ratios measured in eluate fractions collected from two flow-through cleaning procedures. The left column represents a procedure that only cleans for oxide coatings using hydroxylamine (HYDRX). The right column represents a procedure that cleans for the oxide coating and a "refractory" phase, through use of DTPA (see text). The exponential shape of Mn/Ca during the HYDRX reflects removal of the "coating" phase. With removal of only the "coating" phase, the La/Ca in the dissolved foraminifera (in the Weak Acid, W.A., stage) shows a tendency to increase (shown by gray symbols in left column). With removal of both the "coating" and "refractory" phases, the La/Ca in the dissolved foraminifera show distinct "plateaus" corresponding to similar features for Sr; Mg/Ca (Fig. 7; shown by gray symbols in right column). These data suggest that REEs are highly enriched in the "refractory" phase versus the "coating" phase as previously thought.

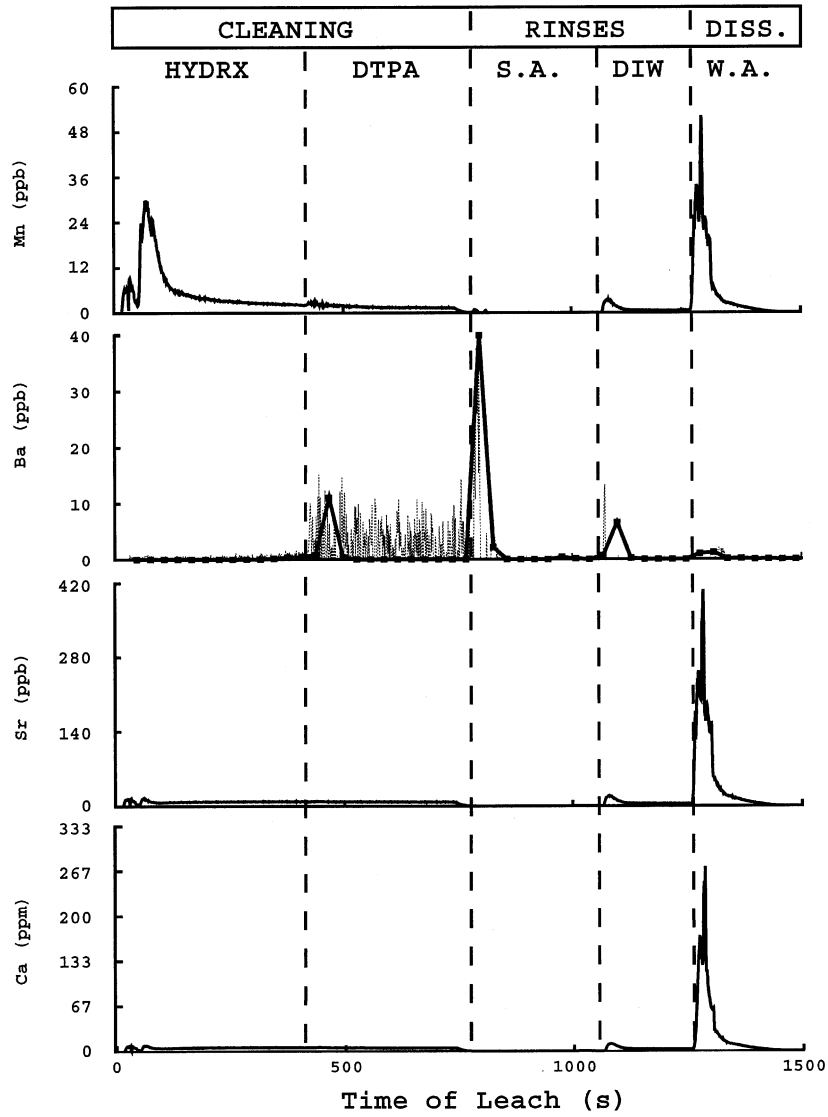

Fig. 3. S.A. = strong acid; W.A. = weak acid; DIW = deionized water. TRA of the total cleaning, rinsing, and dissolution of a foraminiferal sample. Ba frame also shows Ba measured in fractions collected (bold line with square symbols). The "coating" phase is removed in the first stage of cleaning, demonstrated by the Mn curve. The "refractory" phase is removed in the second stage of cleaning, demonstrated by the loss of Ba. The large Ba spikes during the rinsing stages reflect the tendency of this element to adsorb onto the system walls. Because the eluate has no detectable concentrations prior to the dissolution stage, the system and sample are thought to be cleaned. These data were collected in real time as the procedure ran, demonstrating a key feature of the flow-through system: the ability to completely monitor cleaning and dissolution.

elements by rinsing the system thoroughly before dissolving the sample. Rinsing takes place in two separate stages: first, the system is rinsed with 0.5 M HNO_3 (eluant E3) with V5 in the OFF position to prevent dissolution of the sample. Second, the sample is rinsed with deionized water (DIW; eluant E4) with V5 in the ON position. The need for this rinsing can be seen in Fig. 3; it is best demonstrated with barium, which readily adsorbs at high pH. After an initial spike, the concentrations in the rinsing eluant drop below detec-

tion limits. This indicates that the system and the sample, after the DIW rinse, are clean and ready for the dissolution phase of the procedure. A final note regarding cleaning and rinsing is that the DTPA step, even at high pH, remains quite corrosive to calcite. Cleaning with DTPA was found to be necessary for measurement of Ba (Lea and Boyle, 1993) and the REEs (see Section 4). To avoid unnecessary loss of calcite, this cleaning step should be kept as short as possible while fully cleaning the sample, to the point of exclusion if there is no observed benefit (e.g., for measurement of Mg/Ca ratios).

Finally, the cleaned sample is dissolved using 0.1 M HNO_3. This is done by programming the gradient pump to mix the 0.5 M HNO_3 (E3) and the DIW (E4) in a 1:5 proportion. The dilution process demonstrates the ease with which experimental parameters can be adjusted, as conditions require. For example, preliminary results (not shown) demonstrate that the calcite of different foraminiferal species dissolves at different rates, which is what is observed with dissolution in the ocean.

After dissolution, the sample column is discarded. Plans are underway to automate the column system for multiple samples using a six-position valve.

3. System observations

Before results are discussed, there are three important observations that should be made about this system and the method described. They are (1) that two cleaning steps are sufficient; (2) that this system is in steady state; and (3) that complete monitoring of the process is possible.

Similar to the principles used in batch method cleaning, as few reagents as necessary are used to clean the foraminifera thoroughly. The foraminifera are generally determined to be clean when there is no change in the ratios measured upon dissolution (e.g., Hastings et al., 1998; Martin et al., 1999). For example, flow-through cleaning programs initially included a final hydrogen peroxide cleaning stage. Eventually, however, it was found that there was no difference between these final dissolved elemental ratios and those that did not include an H_2O_2 stage. As a result, the H_2O_2 stage was eliminated from the final procedure. This does not mean that the H_2O_2 would not be useful for other samples, or for other elements (not investigated herein). For example, H_2O_2 may well be necessary for plankton tow or cultured samples. The ability to investigate, then include, or exclude reagents with the flow-through method, is easily accomplished, as the system is very adaptable.

Because the system is flow-through, the sample is always in contact with "fresh" reagent such that the resulting reactions occur at steady state. In batch methods, even after considering the large reagent-to-sample volume ratio, the reactions taking place tend to approach equilibrium. This is not the case in flow-through. Cleaning by flow-through is more efficient and the method is unaffected by differences in sample size or extent of sample contamination, *provided* that the amount of reaction time is sufficiently long. This can be illustrated by the similarity in the amount of time it takes to dissolve sample sizes that differ by an order of magnitude (Fig. 4). As a result, the amount of time given to each cleaning stage errs on the side of being "too long." The benefit of being in steady state is that cleaning and dissolution are predictable and regulated to a high degree of accuracy, regardless of variability between samples.

A major feature of this method is that nothing is lost. That is, the eluates from the cleaning, rinsing, and dissolution stages can be measured and the whole procedure can be monitored. In batch methods, these results are much more difficult and impractical to attain. (Although much valuable insight was gained in the attempts made by Bender et al., 1975; Lea and Boyle, 1993; Brown and Elderfield, 1996, these studies report data only from the final dissolved foraminifera after partial dissolution). The ability to monitor the whole process has been significant in the development of this system, allowing direct observation of the effectiveness of the cleaning process, which can then be adjusted as required. In fact, the ability to monitor and change the system is ideal. Constant flow in the system provides temporal information during the cleaning, rinsing, and dissolution process. It is then the user's option as to what temporal resolution is desired. In the development of this procedure, the typical resolution was a sample every 0.7 min, the time for collection of one fraction. At the highest resolution, the eluate flow can be directed into the ICP-MS, where TRA software allows measurements of elements at millisecond-time scales

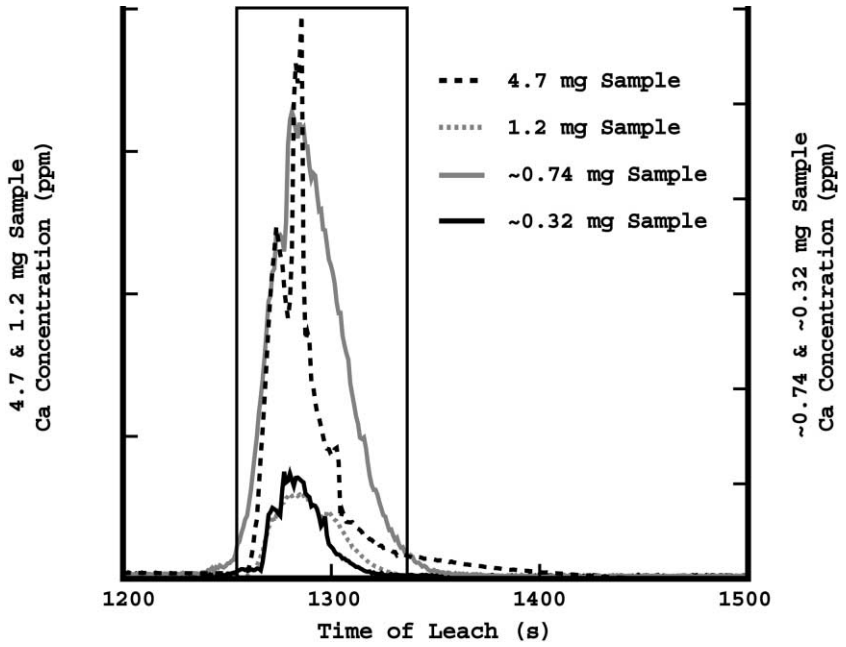

Fig. 4. TRA of eluate directly from the cleaning system into the ICP-MS, during the final dissolution stage of the procedure for four separate samples of different sizes. Although the samples vary an order of magnitude in size, they all dissolve in the same window of time. This provides evidence that the system is in steady state. Therefore, variability in sample size and extent of contamination are not issues in flow-through cleaning and dissolution.

(see example in Fig. 3 or Fig. 8) . At the other end of the spectrum, the whole cleaning and rinsing process may be unmonitored and only the dissolution stage collected. In fact, for routine work this latter option may be preferable for two reasons. First, injecting large amounts of cleaning reagent into an ICP-MS is undesirable, as these reagents constitute a very poor matrix for measurement in the ICP-MS. Second, the trade-off for these high-resolution analyses is that the elements of interest must be sufficiently concentrated for detection by the ICP-MS. Therefore, minor elements, such as magnesium or strontium, may be readily measured using TRA, but trace elements, such as the REEs, may not be sufficiently concentrated in the eluate flow for TRA detectability.

4. Results

Because the flow-through system allows the whole procedure to be monitored over time, greater insight into the cleaning process is gained. Some of these results follow previous work; other results have been unexpected and may prove to be crucial in future paleoceanographic studies. This paper focuses on results that demonstrate the features of this new method. However, some results pertaining to the nature of the chemistry of *Orbulina* shells will be discussed in a cursory manner, in order to highlight features of foraminiferal calcite that, this new method may be able to expose.

As shown in the previous section, thorough cleaning of foraminiferal calcite requires a two-stage chemical cleaning process to remove two distinctly different contaminant phases. These phases are the ‘‘coating phase,’’ a highly recognized metal oxide coating that forms on the shells (e.g., Boyle, 1981), and the ‘‘refractory phase,’’ a less understood phase that is seldom targeted in batch cleaning methods (Lea and Boyle, 1993). These two phases are enriched with minor and trace elements in differing proportions (few examples are demonstrated in Fig. 5). ‘‘Coating’’ phase elements, those enriched in the oxides, include manganese, cadmium, and magnesium. ‘‘Refractory’’

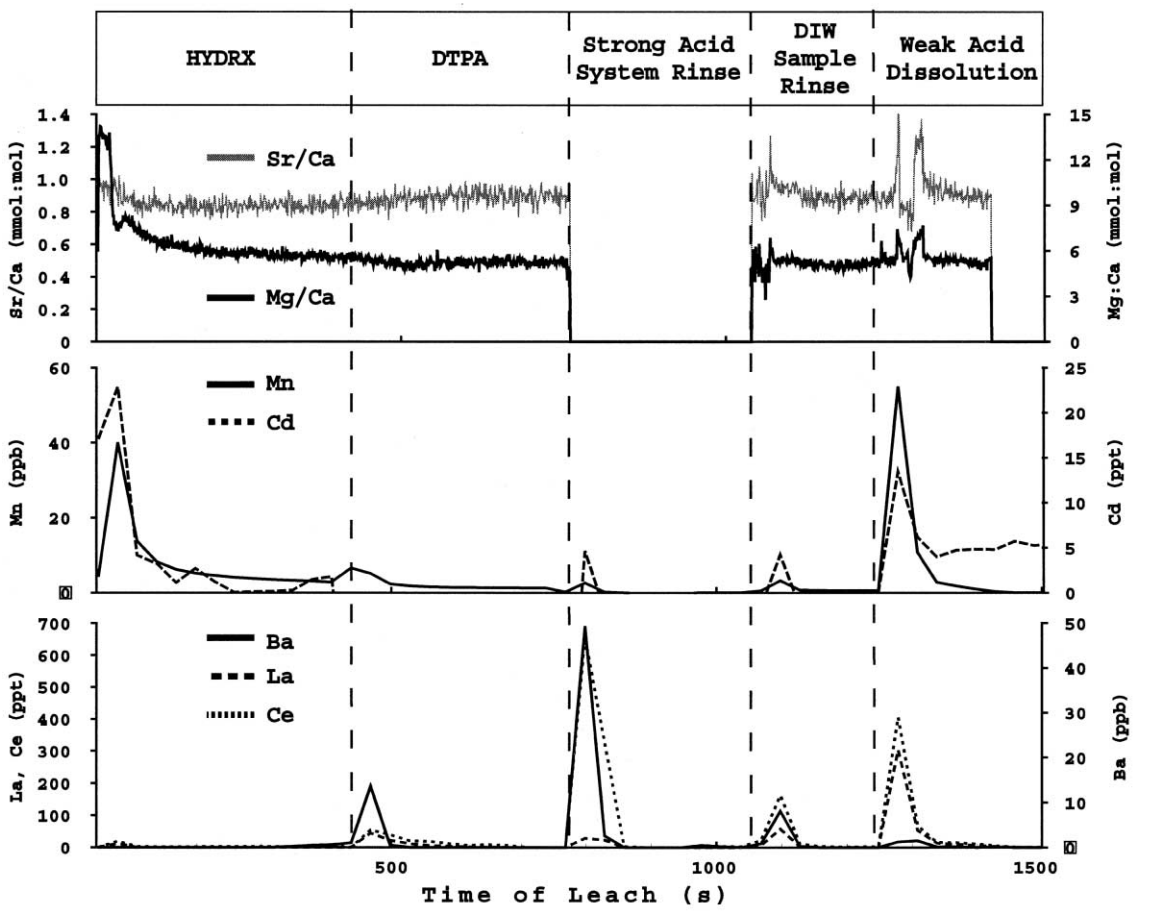

Fig. 5. Complete analyses of total cleaning and dissolution of a foraminiferal sample. TRA on the minor elements (Sr and Mg) is possible in real-time, at the same time discrete fractions are collected for post-run analyses of trace elements. Minor and trace element contamination falls into three categories, corresponding to the phase enriched in the element. The ''coating'' phase is enriched in Mg and Cd, as well as Mn. This phase is a relatively insignificant source of REE contamination compared to the ''refractory'' phase. Other elements, such as Pb (not shown) are found in both contaminant phases.

phase elements, those enriched in the refractory phase, include barium and the REEs. There are other elements, such as lead, that are enriched in both phases.

Because the coating is thought to be a ferromanganese oxide, it is not surprising that Mn is enriched in this phase. This allows the use of Mn as a ''phase indicator'' for the coating phase, and the manganese spike at the start of cleaning indicates that the oxide coating is being removed (Figs. 2, 3 and 5). In future developments of this system, it is conceivable that trace elements may be measured during the coating phase removal and the trace elements from this phase will be isolated through use of the Mn phase indicator.

Similar to Mn, cadmium enrichment in the oxide coating is well-documented (e.g., Boyle and Keigwin, 1987; Martin and Lea, 1998) (Fig. 5). However, unlike Mn and Cd, magnesium enrichment in the oxide coating has been the subject of some debate (e.g., Hastings et al., 1996; Elderfield and Ganssen, 2000). These flow-through data support the view that there is a significant Mg enrichment in the coating phase (Fig. 5), which indicates that measuring accurate Mg/Ca ratios in foraminiferal calcite requires cleaning for the coating phase at the very least.

On the other hand, contrary to previous results suggesting that the REEs are enriched in the ''coat-

ing'' phase (Palmer, 1985; Palmer and Elderfield, 1986), flow-through results demonstrate that this phase is only a minor contributor to REE contamination. By far, the most REE-enriched phase is the ''refractory'' phase. This is shown in two ways. First, there is a spike of REE in the eluate as the DTPA

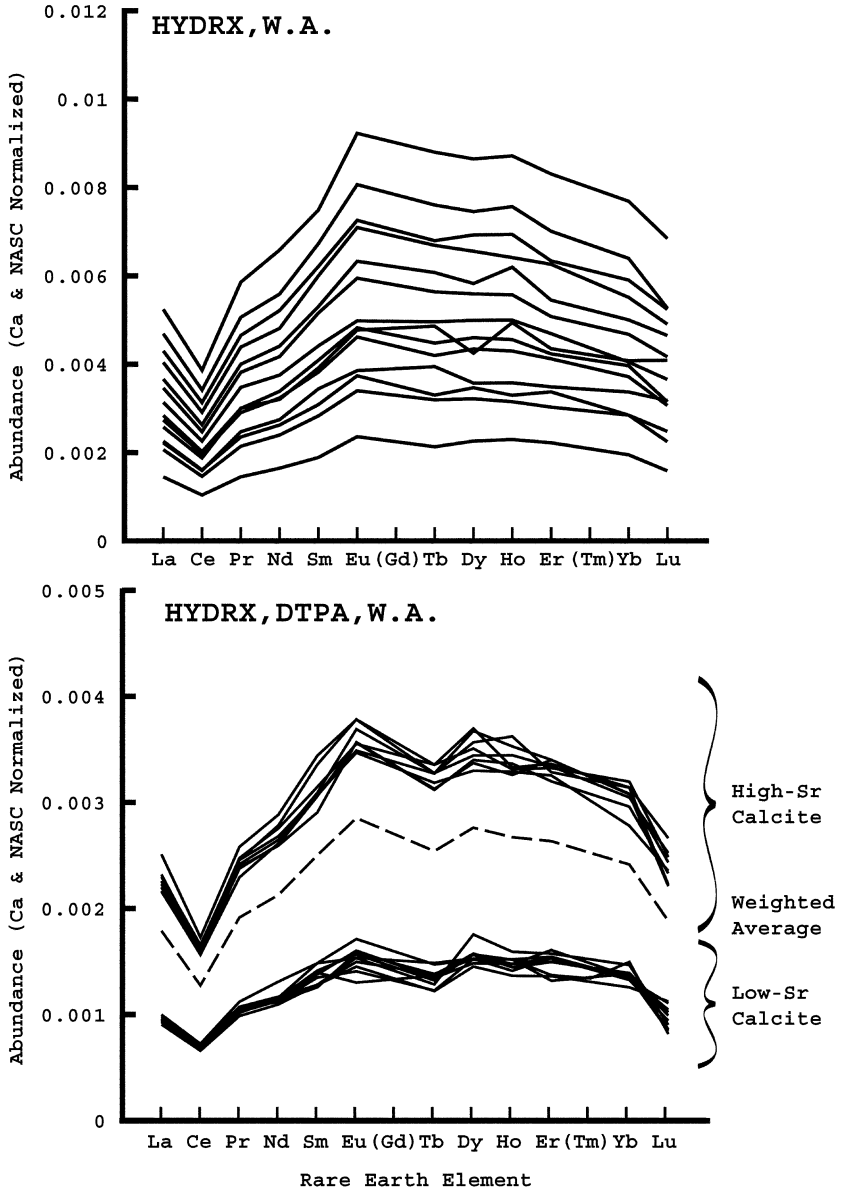

Fig. 6. REE patterns, normalized to calcium in the eluate, and to a shale standard (NASC), measured in eluant fractions from the dissolution stage of the foraminifera sample. Gd and Tb are not included, as these data are prone to inaccurate analyses in quadrupole ICP-MS. Upper panel data is from a sample that has only been cleaned for ''coating'' phase contamination. Lower panel data is from a sample that has been cleaned for both the ''coating'' and ''refractory'' phases. Removal of this latter phase is important in cleaning for REEs. The distinct REE patterns in the lower panel reflect the two calcite types seen in minor element/calcium ratios.

cleaning stage begins (Fig. 5). Because there is no pH change at this time, this REE spike cannot be attributed to rinsing of adsorbed REEs from the coating. Second, the REE/Ca values measured in dissolving foraminifera that have not been cleaned for the refractory phase have been found to increase (bottom-left panel in Fig. 2). To explain this trend away as readsorption (Sholkovitz, 1989) would require the REEs to readsorb onto the dissolving foraminiferal shells in a 4 ml/min flow of acid. Instead, these data seem to indicate a mixing curve between a lower REE/Ca phase (the readily dissolved foraminifera), and a high REE/Ca phase (the more resistant "refractory" phase). The fact that the REE/Ca in the dissolved foraminifera that *have* been cleaned for the refractory phase are constant (bottom-right panel in Fig. 2) indicates that there is a refractory phase contamination problem, whereas there is no obvious way to reconcile readsorption with these data.

Finally, the REE patterns (Fig. 6) clearly show the importance of removing the refractory phase. When the refractory phase is not removed, the patterns in fractions of the dissolved foraminifera, although resembling a seawater pattern (e.g., Elderfield and Greaves, 1982; Elderfield, 1988; Piepgras and Jacobsen, 1992), are significantly different from one another (top panel in Fig. 6). On the other hand, when cleaned for the refractory phase, the REE patterns measured in fractions of dissolved foraminifera both resemble seawater and are tightly clustered in two groups (bottom panel in Fig. 6). The potential importance of these two groups will be discussed next.

A most important feature of this flow-through system, as alluded to above, is that the cleaned sample

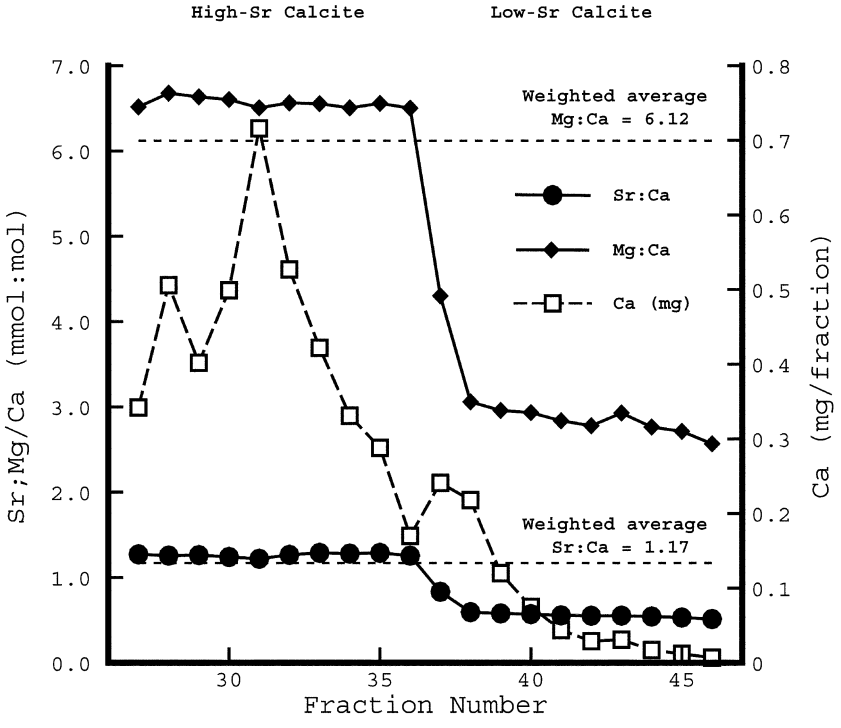

Fig. 7. Fractions collected during the dissolution stage of the flow-through procedure. The dissolution of the sample is shown by the Ca concentration measured in the eluant fractions, which decrease as the sample dissolves away. Unlike the variability in the Ca concentrations, Sr/Ca and Mg/Ca values measured in the fractions appear to have two distinct "plateaus". These "plateaus" only become apparent with slow dissolution and measurement, afforded by the flow-through system. The "plateaus" are apparent in all other minor and trace elements, and may be a significant feature of foraminiferal calcite (see text).

Table 4
Comparison of flow-through results with batch-cleaned results

	Typical planktonic range[a]	Lea et al. (1999), *Orbulina*		Palmer (1985), bulk foraminifera		Element/calcium ratios for *Orbulina* measured with flow-through dissolution		
		Cultured	Core tops[b]	"non-detrital"	"lattice"	"High-Sr" calcite	"Low-Sr" calcite	Weighted average[c]
Sr/Ca (mmol/mol)	1.2–1.6	1.21–1.40	1.64–1.70	–	–	1.26	0.58	1.17
Mg/Ca (mmol/mol)	0.5–5	5.89–13.85	3.17–7.55	–	–	6.57	2.96	6.12
La/Ca (μmol/mol)	<1	–	–	1.26	0.124	0.68	0.28	0.53

[a] Range from Lea (1999).
[b] From references cited in Lea et al. (1999), Bender et al. (1975), Delaney et al. (1985), Rosenthal and Boyle (1993) and Russell et al. (1994).
[c] Weighed averages were done by weighing the "high-Sr" and "low-Sr" calcite ratios by the amount of calcium measured in those fractions. The "high-Sr" calcite accounted for 87.5% of the total calcium presented in Fig. 7. The "low-Sr" calcite accounted for 12.5% of the total calcium presented in Fig. 7. See text for details.

is not dissolved in one aliquot. Therefore, whereas batch-method cleaning allows only one measurement to a given sample, flow-through allows multiple analyses of the foraminifera as it dissolves over time. That is why the strength of the dissolution acid is crucial. A dissolution period, lasting as long as possible, is key to multiple analyses for a given sample, but enough material must be dissolved per unit of time in order to measure the minor or trace elements in the eluate. In some of the earlier experiments, the acid strength was far too strong, dissolving the foraminifera too quickly. However, when the acid strength was adjusted, the need for tight control over the dissolution of the sample became apparent. This is because foraminiferal calcite is not homogenous, even with respect to minor elements such as strontium, as shown in Fig. 7 and pointed out by previous investigations (e.g., Lorens et al., 1977; Brown and Elderfield, 1996; Jha and Elderfield, 2000). The Sr/Ca ratio in *Orbulina*, for example, appears to be comprised of discrete high-Sr and low-Sr types (also implied in Lohmann's, 1995 model) (Fig. 7). Other elements such as Mg, Mn, REEs, follow this pattern, as discussed above for the REEs (Figs. 2 and 6). The chemically distinct Sr "plateaus" in *Orbulina* shells do not reflect the variability in calcium loss during dissolution (Fig. 7); thus, the plateaus must be a robust feature of the calcite of this species, and not an artifact. Further evidence suggest this is true: (1) all the data presented in Fig. 7 are well above detection limits (Table 3), (2) the REE patterns associated with both types of calcite resemble seawater and not a "blank" pattern for the weak acid reagent (enriched in the light REEs). The interpretation of these plateaus will be discussed later. High-Sr calcite accounts for the majority of the sample (>60%) and always dissolves first (Fig. 7) (McCorkle et al., 1995; Brown and Elderfield, 1996). However, if the dissolution acid is too strong, the plateaus are lost, resulting in an intermediate, element/calcium ratio equivalent to the weighted average ratio. In this case, the ratio closely resembles that obtained by batch method dissolution. For example, the weighted averages of the Sr/Ca and Mg/Ca (weighted by mass of calcium in that fraction) are given in Table 4 and shown in Fig. 7. While convenient for comparing to batch method results, this weighted average is problematic for paleoceanographic applications, as discussed subsequently.

5. Discussion

Several observations have been made about the shell chemistry of *Orbulina*. This paper was not intended to be a detailed study of shell chemistry, but an introduction and verification of a new method in paleoceanography. As such, it will be recognized that there is a great deal of development work left to be done with respect to understanding foraminiferal shell chemistry. For example, preliminary results from flow-through have shown distinct differences in different foraminiferal species apparently related to their ecology. Rather, the main objective of this work is to develop a standardized method of thoroughly cleaning

foraminifera for use in paleoceanographic studies. In this regard, the main question must be: are the foraminifera totally cleaned at the end of this procedure? The observation that trace element/calcium ratios reach the same ''plateaus'' as minor elements is a strong indication that they are, in fact, clean (Figs. 2 and 7). Further support for this conclusion is seen from the tight grouping of the REE patterns in both the high and low Sr calcites, which both demonstrate typical seawater patterns (Fig. 6). Finally, the element/calcium ratios in the dissolved foraminifera obtained from this flow-through process are similar to the values obtained in batch methods (e.g., Bender et al., 1975; Boyle, 1981; Palmer, 1985; Lea and Boyle, 1993; Martin et al., 1999; Table 4).

Unfortunately, a comparison of results from batch methods may not be a good test of flow-through cleaning, for two reasons. First, in some cases the cleaning done previously in batch methods has been incomplete; an example of this is the lack of a cleaning stage to remove the refractory phase when cleaning for REEs. Second, a complication arises from the presence of more than one type of calcite in the cleaned foraminiferal shells, i.e., the high-Sr calcite and the low-Sr calcite (Fig. 7). Batch dissolution does not differentiate elemental ratios associated with different calcite types.

Because the contaminant phases as seen in flow-through cleaning appear to be almost devoid of Sr (Fig. 5), and because of the ease of measurement of this minor element, Sr is considered the ''phase indicator'' for calcite. Therefore, although all other elements appear to change concentration in the calcite concurrently with the transition of the high- to low-Sr calcite, it is easiest to determine this change using Sr. This is important because high-Sr calcite, which comprises the bulk of the *Orbulina* foraminiferal sample, dissolves more readily (Fig. 7) (Lorens et al., 1977; McCorkle et al., 1995; Brown and Elderfield, 1996). Direct observation from the flow-through method that this calcite is more likely to dissolve first may be the key in resolving problems associated with natural oceanic dissolution, which occurs above the lysocline for some species (e.g., Lorens et al., 1977; McCorkle et al., 1995; Brown and Elderfield, 1996).

The most pressing dissolution problem is the use of Mg/Ca ratios as a paleothermometer. In batch methods, the cleaned foraminifera represent a weighted average of high-Sr calcite Mg/Ca and low-Sr calcite Mg/Ca values. Natural dissolution of the more susceptible high-Sr (high-Mg) calcite will alter the final weighted average of Mg/Ca in the foraminiferal sample and will result in inaccurate temperature estimates. The flow-through dissolution method can be used to determine the Mg/Ca ratios of all calcite fractions, improving estimates of paleotemperature. This issue is probably important for other paleotracers, such as the REEs, which show distinct patterns between the high-and low-Sr calcites. In the extreme case, this uncertainty might extend to carbon and oxygen isotopes (Lohmann, 1995).

It must be emphasized that the foraminifera used in the development of this system have been *Orbulina*, a rarely used species in paleoproxy studies. In order to fully understand what the differences in calcite may reflect it will be necessary to investigate the shells of other species from core tops, plankton tows, and culturing experiments (e.g., Mashiotta et al., 1997; Lea et al., 1999).

As a preliminary step in this direction, the gradual dissolution of *Globeriginoides sacculifer*, a species more common in paleoceanographic studies, is shown in Fig. 8. These data are presented here to demonstrate that the calcite of many foraminiferal species, not just *Orbulina*, is complex. A complete discussion of these and other data will be presented elsewhere, as the intention of this paper was simply to present the flow-through method and the results found during its development. However, in this regard, several points should be made from the data presented in Fig. 8. First, the similarity of the element/calcium ratios given with multiple isotopes (^{25}Mg, ^{26}Mg, ^{43}Ca, ^{48}Ca, ^{86}Sr, ^{87}Sr) demonstrate that a changing signal caused by matrix changes (i.e., decreasing calcium) is not a significant problem in TRA measurements. Second, the system provides very reproducible results when applied to duplicate samples. The element/calcium ratios shown represent the average (bold line) and the standard deviation (thin lines) of four splits of the same sample (*G. sacculifers* from TT9108-1GC, 185–190 cm depth, averaging 2.9 mg each; Table 5). Third, the weighted average Mg/Ca value calculated from the flow-through experiment agrees well with those found by Hastings et al. (1998), for batch cleaned and dissolved *G. sacculifer* from this core and depth (Table 5). However, only flow-through

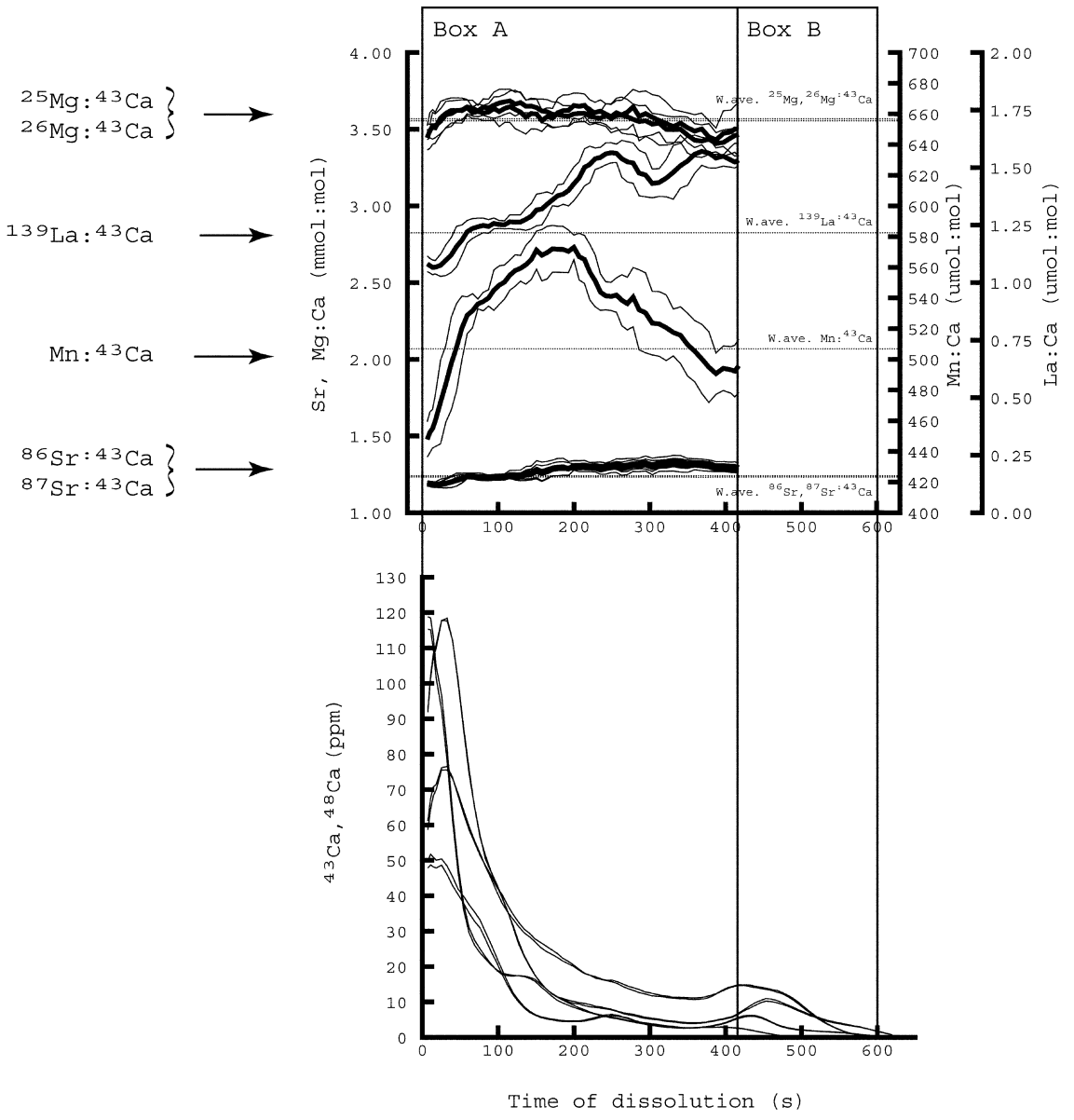

Fig. 8. Four repeat analyses of a split sample of *G. sacculifer* from Caribbean Core TT9108-1GC (185–190 cm depth). Sample sizes were: 2.9, 2.1, 2.6, and 4.1 mg. Only final dissolution stage is shown as TRA data. Box A bounds the data used to calculate the element/calcium ratios. Box B bounds the time for total dissolution of the sample-splits. Although the total dissolution lasts ~ 600 s, the amount of data available for calculating element/calcium ratios is limited to ~ 420 s. This is because the concentration on the isotopes of both minor and trace elements falls below detection limits (presented in Table 2). More data may be acquired from the total dissolution through measurement of fractions collected on a high-resolution ICP-MS (not done). Upper panel: element/calcium ratios. A five-point average was done for the TRA data from each of the four sample-splits, to remove higher frequency instrument noise. The average and standard deviation of this smoothed data for all four sample-splits is plotted for the following elements: Mg/Ca and Sr/Ca (two isotopes for each are shown), Mn/Ca and La/Ca. The weighted average (W. ave) of each is given as a dashed line. Lower panel: calcium profiles. The five-point average was done for the TRA data of both ^{43}Ca and ^{48}Ca. The concentrations determined by the two isotopes agree very well. The pattern and timing of dissolution is similar for all four sample-splits.

Table 5
Values from data presented in Fig. 8

	$^{25}Mg/^{43}Ca$ (mmol/mol)	$^{26}Mg/^{43}Ca$ (mmol/mol)	$^{55}Mn/^{43}Ca$ (μmol/mol)	$^{86}Sr/^{43}Ca$ (mmol/mol)	$^{87}Sr/^{43}Ca$ (mmol/mol)	$^{139}La/^{43}Ca$ (μmol/mol)
Weighted average	3.57	3.58	506.80	1.22	1.23	1.22
Minimum value measured	3.41	3.43	447.78	1.18	1.18	1.07
Maximum value measured	3.66	3.68	573.02	1.31	1.34	1.58
Hastings et al. (1998)	3.34, 3.50		–	–	–	–
Standard deviations (%)						
Average	4.8	4.8	6.1	4.4	4.9	8.1
Minimum	2.1	2.0	1.2	0.9	0.8	2.8
Maximum	6.9	10.0	12.2	8.2	9.7	15.8

gives a complete picture of the variability that makes up the weighted average and sorts the calcite by its susceptibility. This information is crucial when shells undergo partial dissolution post-mortem.

6. Conclusions

A novel method for flow-through cleaning has been presented. This flow-through method has many advantages over traditional batch methods and has produced results that were heretofore unknown. In fact, some of these results were made possible only through the use of the flow-through method.

Most importantly, the system efficiently cleans foraminiferal samples for use in paleoceanographic studies. Other key aspects of the system are as follows.

(1) The system is in steady state, due to constant replenishment of "fresh" reagent over the sample. As a result, differences in extent of contamination between samples are no longer variables, as in batch methods.

(2) The system is automated and fully enclosed. This reduces contamination and potential problems associated with differences in cleaning efficiencies among laboratories, as the same procedure could be reproduced consistently everywhere at the same operating conditions.

(3) The system is highly flexible, permitting effective investigation and incorporation of changes in cleaning methods as they are discovered. In fact, this may become an important feature if it is found that foraminiferal calcite is as chemically variable as this and other studies suggest (e.g., Bender et al., 1975; Brown and Elderfield, 1996; Jha and Elderfield, 2000).

(4) Continuous analyses of the total cleaning and dissolution procedures are possible because nothing is lost from this system. Such a feature has proved invaluable in development of this cleaning procedure and it will likely become much more important with improvements in TRA and other ICP-MS technologies.

(5) Cleaning the refractory phase is crucial for certain elements, such as the REEs. Cleaning for the oxide phase is equally important for other elements, such as Cd and Mg.

(6) The slow dissolution in the flow-through method permits multiple measurements of a single sample, as opposed to the single measurement obtained from batch dissolution. This feature allows for the assignment of error bars on paleotemperatures from Mg/Ca ratios, for example.

(7) The fact that the flow-through cleaned foraminifera are dissolved over time (versus all at once in the batch method) has produced the result that the *Orbulina* foraminifera shell is composed of two types of calcite: one with high-Sr and one with low-Sr. Although Sr is used as the "phase indicator," other minor and trace elements act similarly. The reason for this should be investigated further, as it may be crucial for future paleotracer work with all species of foraminifera.

Although the system is ready for use now, there are a few immediate improvements which should be made. Other innovations will undoubtedly follow with time and more experience with the system. Current improvements needed are as follows.

(1) Optimal dissolution acid strength for the foraminiferal species types should be determined. This ought to balance the need for measurable concentra-

tions of minor and trace elements with the desire for as many measurements as possible of a given sample.

(2) The use of hydrazine as a cleaning reagent for the oxide coatings should be investigated. Because this reagent may be more efficient than hydroxylamine, it may prove to save time and reagent spent on cleaning.

(3) The system should be re-plumbed to accommodate multiple sample columns. In this way, it can be programmed to clean several samples in one run.

In summary, the flow-through system described herein will be beneficial in the growing field of proxy work in paleoceanography with respect to:

1. accuracy, reliability, and reproducibility of cleaning;
2. high resolution down-core investigations requiring large numbers of cleaned samples; and
3. recent concerns about foraminiferal calcite heterogeneity, and what this implies about the effect of partial dissolution on the seafloor.

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