Accuracy, standardization, and interlaboratory calibration standards for foraminiferal Mg/Ca thermometry

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[1] The use of liquid and solid standards for foraminiferal Mg/Ca and Sr/Ca determinations and interlaboratory calibration has been investigated. Preparation of single element standard solutions from primary solid standard material enables the preparation of mixed standard solutions with Mg/Ca and Sr/Ca ratios of known accuracy to better than 0.1%. We also investigated commercial reference materials to determine whether existing carbonate standards could be used as reference material for Mg/Ca determinations in foraminiferal calcite. We propose that, in the absence of a pure calcium carbonate standard certified for Mg/Ca, ECRM 752-1, a limestone CRM containing Mg/Ca within the range of typical foraminifera, is a suitable solid standard for interlaboratory calibration. Replicate Mg/Ca determinations showed that, provided silicate phases are removed by centrifugation, this material is homogenous within the precision of daily instrumental Mg/Ca determinations over a range of sample weights from 10 to 1000 mg, taken from two separate bottles of ECRM 752-1. Results gave an average value of Mg/Ca = 3.75 mmol/mol (0.015 s.d., 0.41% r.s.d.) on 118 determinations from the two bottles.

1. Introduction

[2] Reliable estimates of marine palaeotemperature are crucial to understanding the ocean-climate system in the geological past. Magnesium/calcium ratios in foraminiferal calcite show a temperature dependence due to the partitioning of Mg during calcification and, during recent years, Mg/Ca ratios in foraminiferal calcite have become established as a palaeotracer of ocean temperature [*Nurnberg et al.*, 1996; *Hastings et al.*, 1998; *Lea et al.*, 1999, 2000; *Elderfield and Ganssen*, 2000; *Mashiotta et al.*, 1999; *Rosenthal et al.*, 2000; *Dekens et al.*, 2002].

[3] As foraminiferal Mg/Ca ratios are now routinely analyzed as indicators of past ocean temperatures, comparability of measurements between laboratories has become an important issue. A recent interlaboratory calibration study by *Rosenthal et al.* [2004] evaluated the reproducibility of results within and between laboratories, both for the analyses of foraminiferal samples and of synthetic standard solutions. The study demonstrated

that for analyses of synthetic standard solutions, within laboratory instrumental precisions better than 0.5% were usually obtained for both Mg/Ca and Sr/Ca measurements, but interlaboratory precisions (r.s.d.) were significantly worse (up to 3.4% and 1.8%, respectively). Interlaboratory precision of about 8% obtained for the measurement of Mg/Ca in foraminifera reflected a combination of interlaboratory instrumental precision and the effect of different cleaning methods used by different laboratories.

[4] It is clear that a number of analytical issues remain. A central conclusion made by *Rosenthal et al.* [2004] highlighted the need for good instrumental intercalibration standards. Synthetic standard solutions are valuable but there are analytical issues in the preparation of accurate element ratio standards and, when distributed between laboratories, the risk always remains that solutions have not retained their initial composition by the time they are analyzed. A solid intercalibration standard would overcome some of these problems, although such a material would itself first need to be calibrated by the community.

[5] In this paper, we address the requirements for and the preparation of accurate analytical standards, and investigate solid reference materials which could be developed for use as robust intercalibration standards.

2. Standard Solutions for Mg/Ca and Sr/Ca Calibration

[6] Standard solutions with accurately known element concentrations and ratios are essential for instrument calibration and for the investigation of matrix effects. The significantly worse interlaboratory precisions, compared to within laboratory precisions, obtained for analyses of circulated standard solutions as reported by *Rosenthal et al.* [2004], could be a result of differences between calibration standards used by laboratories, or because the circulated standard solutions had become contaminated in the interval between their preparation and analyses, or a combination of both.

[7] In most cases, calibration standards are prepared by mixing single element standard solutions to give the required element ratio. The accuracy of the element ratio obtained depends on the errors introduced by the preparation procedure, corrections for interelement contamination and, crucially, the accuracy of the single element standards. Typ-

ically, commercial single element standard solutions are certified to ±0.5% of the quoted concentration but, usually, this applies to the batch prepared by the manufacturer and not to the individual bottle. Concentration errors in single element standards propagate into mixed element standard solutions as systematic errors on the calculated ratios. In order to ensure that concentrations of single element standard solutions were more accurately known before preparing mixtures, we prepared single element standards starting from primary solid materials, as described by *Moody et al.* [1988]. Mixed standard solutions prepared from these are used routinely in this laboratory for Mg/Ca and Sr/Ca determinations by ICP-OES following the method of *de Villiers et al.* [2002]. Standard solution preparation was described briefly by *de Villiers et al.* [2002]; more details are included here.

[8] Calibration solutions were prepared gravimetrically starting from high-purity $CaCO_3$ (NIST SRM 915a), $SrCO_3$ (NIST SRM 987) and Mg metal rod (Newmet Koch, purity 99.9+%) following the criteria recommended by *Moody et al.* [1988]. Before dissolution the carbonate standards were dried to constant weight at 110°C and the Mg metal rod was etched with $\sim$0.1M HNO_3 (and microscopically examined) to remove any oxide coating, then dried under vacuum. The standards were weighed in Pt crucibles and the weights corrected for air buoyancy and the certified assay purity. Single element concentrated standards were prepared in 1 liter Teflon FEP (fluorinated ethylene propylene) bottles, cleaned by soaking overnight in hot 50% HNO_3 then rinsed and dried before use. The carbonate standards were rinsed into the bottles with water, covered with water and dissolved by the slow addition of nitric acid; this procedure prevents powder loss from static and sample loss from effervescence on dissolution. Ultrapure water and nitric acid (quartz distilled) were used throughout. Similarly, the Mg rod was transferred to an FEP bottle, covered with water and dissolved by slow addition of nitric acid. After dissolution the standards were made up with water and acidified to give an acid concentration of $\sim$0.1M HNO_3. Concentrations of the other two elements in each standard solution were measured by ICP-OES. Mg and Sr concentrations in the Ca standard solution were in agreement with concentrations calculated from the NIST 915a certified values, and contributions for these two elements were included in the error propagation calculations when preparing subse-

Table 1. Mg/Ca and Sr/Ca Mixed Standard Solutions

Standard	Mg/Ca, mmol/mol	Estimated Error		Sr/Ca, mmol/mol	Estimated Error		[Ca], μg/g
		mmol/mol	%		mmol/mol	%	
CL 2	0.5059	0.0003	0.06	0.5057	0.0002	0.04	1801
CL 9	0.9083	0.0007	0.07	0.7023	0.0005	0.07	830
CL 3	1.289	0.001	0.05	0.8083	0.0003	0.04	1047
CL 4	2.374	0.001	0.04	1.0633	0.0004	0.04	1002
CL 7	4.048	0.003	0.07	1.615	0.001	0.06	881
CL 1	5.130	0.002	0.03	2.088	0.001	0.03	2088
CL 8	7.509	0.005	0.06	2.835	0.002	0.06	926
CL 5	9.162	0.005	0.06	3.554	0.002	0.06	924
CL 6	18.43	0.01	0.06	7.337	0.004	0.06	891

quent mixtures. Measurement of the Ca and Sr concentrations in the Mg standard solution, and Ca and Mg concentrations in the Sr standard solution confirmed that their contributions would be negligible in the subsequent mixed standard solutions and no corrections were applied.

[9] Mixed standard solutions were prepared containing Mg/Ca and Sr/Ca ratios covering the range observed in foraminiferal calcite. All solutions were prepared gravimetrically in FEP bottles using ultrapure reagents to give solutions in ~0.1M HNO_3. Estimated errors on the Mg/Ca and Sr/Ca ratios were calculated by propagation of the weighing errors and the concentration uncertainties of the single element primary standards [*Miller and Miller*, 1993] to produce a series of concentrated standard solutions each with Mg/Ca and Sr/Ca ratios known accurately to better than 0.1%. Details of the concentrated mixed standards are given in Table 1. Aliquots of these standard solutions for interlaboratory calibration, to complement the standard solutions previously circulated by *Rosenthal et al.* [2004], can be provided on request. On the other hand, it would be preferable to have appropriate solid standards for use as reference material by laboratories.

3. Intercalibration Standard

[10] Synthetic standard solutions are not ideal for interlaboratory calibration because of the difficulty of ensuring their integrity over time. The risk always remains that solutions on analysis have not retained their prepared composition because of either evaporation or contamination during transport and storage. Evaporation, which affects element concentrations equally, is only a minor problem for element ratio standards, whereas contamination affects individual elements unequally and has serious consequences for element ratios.

Plastics such as polypropylene and high-density polyethylene, manufactured catalytically using a polymerization procedure involving $MgCl_2$ supported Ziegler-Natta catalysts [*Masuda et al.*, 1997], represent an obvious contamination risk for Mg/Ca standard solutions. The potential for contamination is minimized by circulating concentrated standard solutions in acid cleaned plastic bottles, but there will always be uncertainty in the integrity of small volumes of standard solutions over time. An ideal reference material for interlaboratory calibration would be a solid standard with well characterized Mg/Ca (and Sr/Ca) ratios, similar to typical foraminifera calcite. This would circumvent the potential problems inherent in the circulation of liquid standards. A series of three reference standards, covering the range of Mg/Ca ratios in foraminifera, would enable analysts to check the sensitivity and linearity of their techniques across the range.

[11] Requirements for any solid standard are that (1) it has Mg/Ca (and Sr/Ca) within the range of foraminifera samples; (2) it is homogeneous, both within and between batch samples; (3) it has a matrix of pure calcite with no contribution to Mg/Ca and Sr/Ca ratios from other mineral phases; and (4) it is readily available in a form suitable for use.

[12] We have investigated commercial reference materials to see whether existing carbonate standards could be used as reference materials for Mg/Ca in foraminiferal calcite. Table 2 lists element concentrations and calculated Mg/Ca and other element ratios for a selection of certified reference materials (CRMs). In general, the Mg concentrations of available calcite and limestone certified reference materials are too high to match foraminiferal calcite, and these materials contain significant Al, Fe, Si and Ti from other mineral phases (Table 2).

Table 2. Certified Reference Materials[a]

CRM	Certified by	Quoted Element Concentrations, wt.%							
		Ca	Mg	Sr	Al	Fe	Mn	Si	Ti
IPT 35	IPT	38.5	0.42	0.034	0.064	0.049	0.01	0.93	0.008
ECRM 701-1	ECISS	37.7	0.36	-	0.29	0.73	0.02	0.93	0.018
SRM 1C	NIST	35.9	0.25	0.025	0.34	0.19	0.02	3.20	0.042
VS W10/2	ICRM	39.9	0.19	-	0.003	-	-	0.02	-
CM 1767	CMSI	39.4	0.14	-	0.03	0.06	-	0.21	-
ECRM 752-1	BAS	39.6	0.093	0.016	0.033	0.016	0.01	0.33	0.005
UN AK	IMRM	39.2	0.066	0.237	0.029	0.045	-	0.30	-
BAM RS3	BAM	40.0	0.018	0.017	<0.001	<0.001	-	-	-

	Material	Calculated Ratios, mmol/mol						
		Mg/Ca	Sr/Ca	Al/Ca	Fe/Ca	Mn/Ca	Si/Ca	Ti/Ca
IPT 35	calcitic limestone	18.1	0.40	2.5	0.9	0.18	34.3	0.17
ECRM 701-1	calcite	15.8	-	11.4	13.9	0.43	35.2	0.40
SRM 1C	argillaceous limestone	11.6	0.32	14.2	3.8	0.39	126.9	0.98
VS W10/2	limestone	8.0	-	0.1	-	-	0.8	-
CM 1767	limestone	6.1	-	1.0	1.0	-	7.6	-
ECRM 752-1	limestone	3.9	0.19	1.2	0.3	0.15	11.9	0.12
UN AK	aragonite	2.8	2.76	1.1	0.8	-	10.9	-
BAM RS3	calcite	0.8	0.20	<0.02	<0.01	-	-	-

[a] IPT, Insituto do Pesquisas Tech. do Estado de Sao Paulo, Brazil; ECISS, European Committee for Iron and Steel Standardisation; NIST, National Institute of Standards and Technology, USA; ICRM, Institute for Certified Reference Materials, Russia; CMSI, China Metallurgical Standardization Research Institute, Beijing; BAS, Bureau of Analyzed Samples Ltd, Newnham Hall, Middlesborough, UK; IMRM, Institute of Mineral Raw Materials, Czech Republic; BAM, Bundesanstalt fur Materialforschung und -prufung, Germany.

[13] Among the certified reference materials listed in Table 2 one standard closely meeting the requirements for foraminiferal calcite is ECRM 752-1 (alternative name BCS-CRM 393), a limestone CRM issued by the Bureau of Analyzed Samples Ltd. UK. The calculated Mg/Ca ratio of ECRM 752-1 is 3.9 mmol/mol, within the range of typical planktonic foraminifera samples. Calculated Al/Ca, Fe/Ca, Si/Ca and Ti/Ca ratios, indicating the presence of contaminant silicate minerals and associated non-carbonate Mg, are low, although higher than observed in cleaned foraminifera [*Barker et al.*, 2003]. The certified element concentrations of ECRM 752-1 are insufficiently precise to permit direct use as a foraminiferal Mg/Ca CRM; propagation of the concentration errors produces a 6.8% (r.s.d.) error on the calculated Mg/Ca ratio. However, if this material is sufficiently homogeneous it has potential as an Mg/Ca consistency standard for use within and between laboratories.

[14] ECRM 752-1 was prepared from a Derbyshire, UK, limestone and is supplied as a powder, ground to pass a 75 μm sieve. Enquiries of the manufacturer confirmed that this material was prepared in a single batch, but is packed according to demand with individual bottles labeled with a packing lot number (Bureau of Analyzed Samples, personal communication). Determination of its Mg/Ca homogeneity, both within the calcium carbonate, and the contribution from accessory mineral phases, is necessary in order to assess its suitability as a reference material for foraminiferal Mg/Ca. We performed homogeneity tests on two separate bottles of ECRM 752-1, taken from the same packing lot number, 0973, using sample weights in the range 0.1 mg to 1000 mg.

3.1. Analytical Methods

[15] Replicate aliquots of 10, 50,100, 250, 500 and 1000 mg were weighed from each of two 100g bottles of ECRM 752-1 into acid cleaned (10% HNO_3, overnight) and dried low-density polyethylene (LDPE) bottles. Samples were dissolved in 0.075M HNO_3 in line with foraminiferal sample preparation. No sample treatment was employed before dissolution. Dissolution volumes were maintained in proportion to sample weights to give constant $[Ca^{2+}]$ of ~400 μg/g (i.e., 10 mg in 10 mL, 50 mg in 50 mL, etc). In the case of smaller sample sizes, 1.0 and 0.1 mg, replicate aliquots were weighed into acid cleaned polypropylene microcentrifuge tubes and dissolved in 1 mL or 0.5 mL 0.075M HNO_3, respectively. The powder dissolved easily, with no particles visible to the naked eye remaining

Table 3. Analytical and Instrumental Conditions[a]

Sample Weight, mg	0.075M HNO$_3$, mL	Dissolution Vessel	[Ca], μg/g
Analytical Conditions			
1000	1000	1000 mL LDPE bottle	400
500	500	500 mL LDPE bottle	400
250	250	250 mL LDPE bottle	400
100	100	125 mL LDPE bottle	400
50	50	60 mL LDPE bottle	400
10	10	15 mL LDPE bottle	400
1	1	1.5 mL PP microcentrifuge tube	400
0.1	0.5	0.5 mL PP microcentrifuge tube	80
All solutions diluted to constant Ca concentration for analysis			60

Category	Parameter	Setting
Instrument: Varian Vista Simultaneous ICP-OES		
Plasma	Configuration	Axial
	RF power	1.2 kW
	Plasma gas flow	15 L/min
	Auxiliary gas flow	1.5 L/min
	Nebulizer gas flow	1.0 L/min
Nebulizer	Glass expansion, Micromist	0.2 mL/min
Spraychamber	Glass expansion, Cinnabar Cyclonic	
Measurement	Integration time	5 s
	Replicates	6

[a] LDPE, low-density polyethylene; PP, polypropylene.

and solutions were analyzed both with and without centrifugation. 0.5 mL aliquots were centrifuged using an Eppendorf model 5415 C microcentrifuge (10 mins. >= 6000 rpm). Between six and twelve replicate weighings were analyzed after centrifugation at each weight, but not all samples were analyzed without centrifuging. Solutions were diluted to [Ca^{2+}] = 60 μg/g and element ratios determined by ICP-OES using a Varian Vista Axial instrument following the procedure of *de Villiers et al.* [2002]. The analytical and instrumental conditions are summarized in Table 3. Solutions were always analyzed (both with or without centrifugation) on the same day as samples were dissolved, although the entire experiment was performed over a number of days. The instrument was calibrated using the standard solutions described in Section 2. Dilution of samples and standard solutions to constant [Ca] permits instrument calibration using the intensity ratio method, with a Ca concentration of 60 μg/g chosen [*de Villiers et al.*, 2002]. Within run precisions of 0.3% or better were obtained for replicate Mg/Ca determinations of a solution (Q5) containing [Ca^{2+}] = 60 μg/g, Mg/Ca = 5.130 mmol/mol, Sr/Ca = 2.088 mmol/mol and no correction was applied for instrument drift during a run. Daily instrument calibration differences produced mean values for solution Q5 ranging from −0.73% to + 0.30% of its expected Mg/Ca ratio and results were normalized to the Mg/Ca ratio for solution Q5 to account for this variation.

3.2. Results

[16] The Mg/Ca and other element ratios measured in material from the two bottles of ECRM 752-1, using sample weights in the range 10–1000 mg, are summarized in Table 4. The mean Mg/Ca ratios and standard deviations obtained for each set of analyses, including those using smaller sample weights down to 0.1 mg, are plotted against sample weight in Figure 1a.

[17] Results after centrifuging agree well, both within and between the two bottles analyzed, over the range of sample weights from 10 mg to 1000 mg and confirm the homogeneity of Mg/Ca within the readily soluble carbonate material. Inhomogeneity would be indicated by increasing scatter in the data with decreasing sample size but this was not observed, the standard deviations for the sets of analyses remaining similar over the five orders of magnitude weight range (Figure 1a). However, higher Mg/Ca ratios were consistently measured for the smallest sample weights. Small samples, 1.0 and 0.1 mg, were dissolved in polypropylene microcentrifuge tubes and it is likely that sufficient

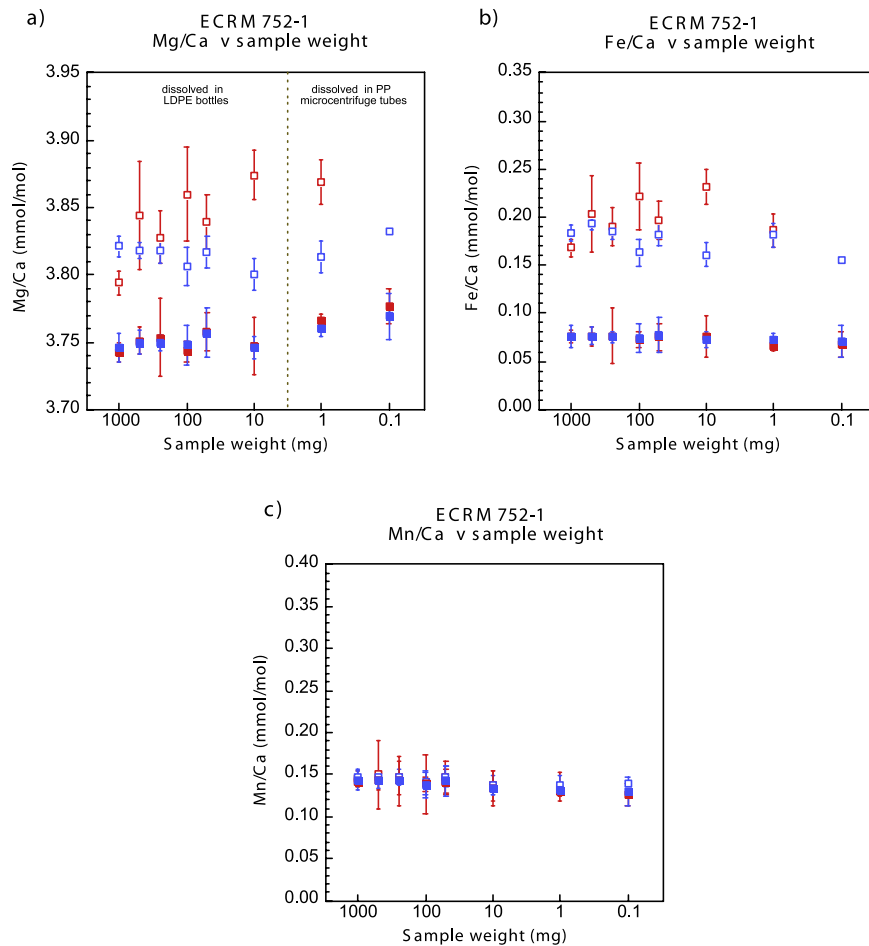**Table 4.** ECRM 752-1: Average Element Ratios Obtained Using Sample Weights in the Range 10–1000 mg[a]

	mmol/mol						
	Mg/Ca	Sr/Ca	Al/Ca	Fe/Ca	Mn/Ca	Si/Ca	Ti/Ca
Not Centrifuged							
Bottle 1							
Mean	3.849	0.189	0.97	0.210	0.143	1.34	0.025
s.d.	0.034	0.002	0.19	0.029	0.006	0.37	0.010
r.s.d., %	0.87	1.29	19.5	13.7	4.2	27.8	40.3
n	34	34	34	34	34	19	34
Bottle 2							
Mean	3.810	0.182	0.74	0.174	0.143	1.08	0.015
s.d.	0.013	0.010	0.17	0.017	0.005	0.22	0.005
r.s.d., %	0.35	5.25	22.6	9.7	3.7	20.2	33.9
n	34	34	34	34	34	34	34
Centrifuged							
Bottle 1							
Mean	3.749	0.189	n.d.	0.076	0.140	n.d.	n.d.
s.d.	0.018	0.004		0.007	0.004		
r.s.d., %	0.47	1.92		9.21	2.83		
n	59	59		59	59		
Bottle 2							
Mean	3.750	0.186	n.d.	0.075	0.141	n.d.	n.d.
s.d.	0.012	0.008		0.003	0.004		
r.s.d., %	0.33	4.47		4.5	3.1		
n	59	59		59	59		
Detection limit			0.13	0.024	0.006	0.049	0.007

[a] Table 4 includes all results obtained using sample weights from 10 to 1000 mg but excludes results obtained using smaller sample weights. Bottle 1 and Bottle 2 were two separate bottles of material, both from packing lot number 0973. n.d., below detection.

Mg was extracted from the polypropylene to produce these higher Mg/Ca ratios. An addition of <0.5 ng Mg to 0.1 mg sample would be required to increase its Mg/Ca ratio from 3.75 mmol/mol, the average for all samples weighing from 10 to 1000 mg, to 3.77 mmol/mol, the average for 0.1 mg. This contribution is within the range of Mg blank values measured in this laboratory for polypropylene microcentrifuge tubes (Eppendorf SafeLok) after acid cleaning.

[18] The differences between results for centrifuged and non-centrifuged samples clearly demonstrate the effect of suspended insoluble material, carried through the nebulizer into the plasma torch, on Mg/Ca ratios. Non-centrifuged samples contain higher and more variable Mg/Ca (Table 4, Figure 1a) consistent with higher Fe/Ca (Figure 1b), demonstrating the presence of other mineral phases in this material. Fe/Ca falls to consistent but non-zero values on centrifugation (Figure 2a), suggesting that Fe is associated both with the readily soluble carbonate and with the insoluble suspended material. In contrast, Mn/Ca ratios (Figure 1c) show very little difference between centrifuged and non-centrifuged determinations. Results for Al/Ca, Si/Ca and Ti/Ca (Table 4) show the pres-

ence of these elements in the suspended material. When analyzed after centrifuging, concentrations of these elements fall close to detection limits by ICP-OES. Detection limits, estimated as three times the standard deviation of the blank were, Al, 0.005 μg/g, Fe, 0.002 μg/g, Mn, 0.001 μg/g, Si, 0.002 μg/g, Ti, 0.001 μg/g, giving element ratio detection limits at $[Ca^{2+}]$ = 60 μg/g of Al/Ca, 0.126 mmol/mol, Fe/Ca, 0.024 mmol/mol, Mn/Ca, 0.006 mmol/mol, Si/Ca, 0.049 mmol/mol, Ti/Ca, 0.007 mmol/mol. As element concentrations approach the detection limits, calculated element ratios become unreliable because of the domination of the intensity signal by baseline noise and any interferences on the measured wavelengths. We therefore used intensity data for these elements to demonstrate the effect on Mg/Ca from non-carbonate phases. Figure 2b shows Mg/Ca plotted against Al intensity, after correction of the Al intensity signal at 396.15 nm for the contribution from 60 ppm Ca in solution. The correlation between Mg/Ca and Al indicates aluminosilicate minerals and also shows differences between the two bottles. Similarly, a plot of Mg/Ca against Si (Figure 2c), after subtraction of the Si intensity of the acid blank, clearly demonstrates the effect of un-dissolved silicate phases on Mg/Ca determina-

Figure 1. Homogeneity of ECRM 752-1, measured element ratios versus sample weight: (a) Mg/Ca, (b) Fe/Ca, (c) Mn/Ca. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution. Red, first bottle; blue, second bottle.
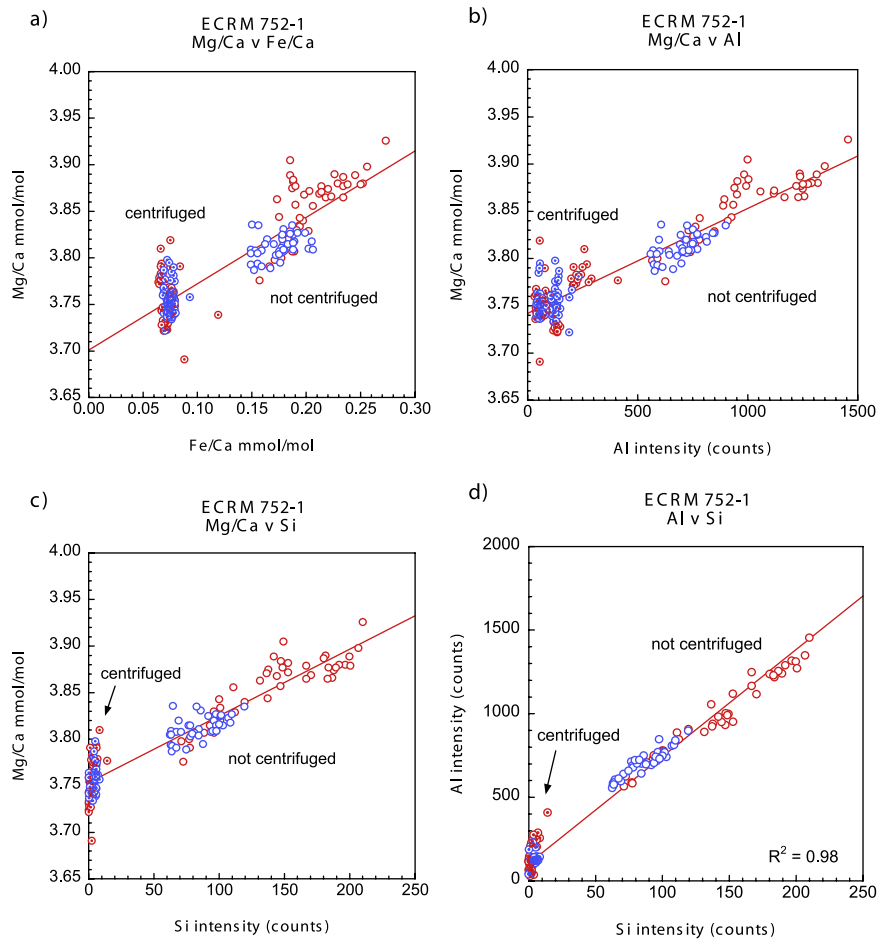
tions. The close correlation of Al with Si (Figure 2d) reinforces this conclusion. The contaminant silicate material must have remained mainly in suspended form to permit centrifugation to lower the Mg/Ca and minor element ratios, but its contribution to the dissolved phase depends on its mineralogy, the acid used and the time interval between the addition of acid and removal of the dissolved phase after centrifuging. The reproducibility of Mg/Ca and Fe/Ca after centifuging (Figures 1a and 1b) implies that any dissolution of contaminant silicate minerals was also reproducible under the conditions used. More detailed experiments would be necessary to quantify the contribution from suspended silicate minerals to the dissolved phase under different conditions.

[19] Measurements of the Sr/Ca ratio (Table 4) of this material confirmed the calculated ratio of 0.19 mmol/mol (Table 2), much lower than Sr/Ca

of 1.0–1.5 mmol/mol typically found in foraminiferal calcite.

[20] Mean measured Mg/Ca ratios of 3.849 mmol/mol (0.034 s.d., 0.87% r.s.d.) and 3.810 mmol/mol (0.013 s.d., 0.35% r.s.d.,) were obtained for 34 determinations from each of the two bottles of ECRM 752-1 when analyzed without centrifugation. The differences in Mg/Ca within and between the two bottles being a result of the contribution of Mg from undissolved aluminosilicate minerals. In comparison, where samples were centrifuged after dissolution, average values of Mg/Ca = 3.749 mmol/mol (0.018 s.d., 0.48% r.s.d.) and 3.750 mmol/mol (0.012 s.d., 0.32% r.s.d.) were obtained on 59 determinations from each of the two bottles of ECRM 752-1 tested.

[21] Measurement precisions more than an order of magnitude better than those calculated from the reference analysis certificate reflect partly the im-

Figure 2. The effect on Mg/Ca of the contribution from insoluble aluminosilicate minerals: (a) Mg/Ca versus Fe/Ca, (b) Mg/Ca versus Al, (c) Mg/Ca versus Si, (d) Al versus Si. Open symbols, not centrifuged; partially filled symbols, centrifuged after dissolution. Red, first bottle; blue second bottle.

proved precision of modern methods, but also the use in this study of a single technique applied to two bottles of material taken from the same packing lot. Investigation of many bottles from more than one packing lot would be expected to give worse reproducibility. However, it is clear from this study (see Figure 2) that the major contribution to inhomogeneity within this material is from contaminant silicate minerals; not visible to the naked eye but visible microscopically as small particles within the powder. Homogeneity of the readily soluble calcite material across many bottles may therefore not be significantly different from that established using the two bottles tested in this study. The dissolution protocol employed is important, the primary objective being to check instrumental calibrations. It is obviously necessary for laboratories to record a batch number and, if discrepancies are found, it would be a simple exercise for collaborating laboratories to exchange material. It is preferable to dissolve a sample

weight in the range 10–100 mg to give a high Ca concentration and analyze an aliquot, rather than dissolving a sample weight more typical of foraminifera analyses, in order to minimize the effect of the Mg blank from small dissolution vials (Figure 1a).

4. Conclusions

[22] Errors involved in the preparation of accurate calibration standards for Mg/Ca and Sr/Ca determinations in foraminiferal calcite represent a significant contribution to interlaboratory analytical precision. To minimize systematic errors in the preparation of mixed standards we prepared initial single element standard solutions starting from primary solid standards. However, the use of standard solutions for interlaboratory calibration is not ideal because of the difficulty of maintaining the integrity of small volumes of liquid standards.

[23] We have investigated commercial reference materials to determine whether there are existing carbonate standards of appropriate composition which could be used as reference materials for Mg/Ca determinations in foraminiferal calcite. In the absence of a pure calcium carbonate standard certified for Mg/Ca, we propose that ECRM 752-1, a limestone CRM containing Mg/Ca within the range of typical planktonic foraminifera, is a suitable solid standard for interlaboratory calibration. Two bottles of this material, from the same packing lot number, were tested for homogeneity with respect to their Mg/Ca ratio. The presence of minor aluminosilicate mineral phases affected the homogeneity of the bulk material but, after removal of these phases by centrifugation the average results for the two bottles tested (Table 4) showed that this material is homogenous within the precision of daily instrumental Mg/Ca determinations over a range of sample weights from 10 to 1000 mg, with Mg/Ca = 3.75 mmol/mol (0.015 s.d., 0.41% r.s.d.) on 118 determinations from the two bottles. This reproducibility is equivalent to an estimated error in Mg/Ca temperature calculation of ±0.1°C. The reproducibility of Mg/Ca ratios confirms the potential of the ECRM 752-1 standard as a reference material for Mg/Ca determinations in foraminiferal calcite, provided that care is taken to remove undissolved contaminant silicate phases before analysis.

[24] We chose to investigate ECRM 752-1 because of its Mg/Ca ratio within the mid-range of planktonic foraminifera and its ready availability. Investigation of other reference materials (Table 2) are necessary to determine how their suitability compares to ECRM 752-1.

Acknowledgments

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