



## Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry

### **M. Greaves**

*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK  
(mg109@esc.cam.ac.uk)*

### **N. Caillon and H. Rebaubier**

*LSCE/IPSL, UMR CNRS, CEA, UVSQ, Bâtiment 12, avenue de la Terrasse, F-91198 Gif sur Yvette, France*

### **G. Bartoli**

*Institute für Geowissenschaften, Kiel University, Olshausenstrasse 40, D-24118 Kiel, Germany*

*Now at ETH Zentrum, Chemie Altbau, CAB E64, Universitätstrasse 6, CH-8092 Zurich, Switzerland*

### **S. Bohaty**

*Department of Ocean Sciences, University of California, Santa Cruz, Santa Cruz, California 95060, USA*

*Now at School of Ocean and Earth Science, University of Southampton, National Oceanography Centre, European Way, Southampton SO14 3ZH, UK*

### **I. Cacho**

*GRC Geociències Marines, Department of Stratigraphy, Paleontology and Marine Geosciences, University of Barcelona, C/Martí i Franquès, s/n, E-08028 Barcelona, Spain*

### **L. Clarke**

*School of Ocean Sciences, College of Natural Sciences, Bangor University, Askew Street, Menai Bridge, Isle of Anglesey, Wales LL59 5EY, UK*

### **M. Cooper**

*National Oceanography Centre, European Way, Southampton SO14 3ZH, UK*

### **C. Daunt**

*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK*

### **M. Delaney**

*Department of Ocean Sciences, University of California, Santa Cruz, Santa Cruz, California 95060, USA*

### **P. deMenocal**

*Lamont-Doherty Earth Observatory, Columbia University, Geoscience 211, Route 9W, Palisades, New York 10964, USA*

### **A. Dutton and S. Eggins**

*Research School of Earth Sciences, Australian National University, 1 Mills Road, Canberra, ACT 0200, Australia*

**H. Elderfield**

*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK*

**D. Garbe-Schoenberg**

*Institute für Geowissenschaften, Kiel University, Olsbhausenstrasse 40, D-24118 Kiel, Germany*

**E. Goddard**

*College of Marine Science, University of South Florida, St. Petersburg, Florida 33701, USA*

**D. Green**

*National Oceanography Centre, European Way, Southampton SO14 3ZH, UK*

**J. Groeneveld**

*IFM-GEOMAR, Wischhofstrasse 1-3, D-24148 Kiel, Germany*

*Now at Research Center Ocean Margins, University of Bremen, D-28359 Bremen, Germany*

**D. Hastings**

*Collegium of Natural Sciences, Eckerd College, 4200 54th Avenue South, St. Petersburg, Florida 33713, USA*

**E. Hathorne**

*Department of Earth Sciences, Open University, Milton Keynes, UK*

*Now at Research Center Ocean Margins, University of Bremen, D-28359 Bremen, Germany*

**K. Kimoto**

*Institute of Observational Research for Global Change, JAMSTEC, 2-15, Natsushima-cho, Yokosuka, 247-0061 Japan*

**G. Klinkhammer**

*College of Oceanography, Oregon State University, Oceanography Administration Building 104, Corvallis, Oregon 97331, USA*

**L. Labeyrie**

*LSCE/IPSL, UMR CNRS, CEA, UVSQ, Bâtiment 12, avenue de la Terrasse, F-91198 Gif sur Yvette, France*

**D. W. Lea**

*Department of Geological Sciences, University of California, Santa Barbara, Mail Stop 9630, Santa Barbara, California 93106, USA*

**T. Marchitto**

*INSTAAR, University of Colorado, Campus Box 450, Boulder, Colorado 80309, USA*

**M. A. Martínez-Botí and P. G. Mortyn**

*ICTA, Universitat Autònoma de Barcelona, Edifici Cn - Campus UAB, E-08193 Bellaterra, Spain*

**Y. Ni**

*Department of Earth Sciences, University of Bristol, Bristol, UK*

*Now at Research Institute of Petroleum Exploration and Development, PetroChina, 20 Xueyuan Road, Haidian District, Beijing, China, 100083*

**D. Nuernberg**

*IFM-GEOMAR, Wischhofstrasse 1-3, D-24148 Kiel, Germany*

**G. Paradis**

*Department of Geological Sciences, University of California, Santa Barbara, Mail Stop 9630, Santa Barbara, California 93106, USA*

**L. Pena**

*GRC Geociències Marines, Department of Stratigraphy, Paleontology and Marine Geosciences, University of Barcelona, C/Martí i Franquès, s/n, E-08028 Barcelona, Spain*

**T. Quinn**

*College of Marine Science, University of South Florida, St. Petersburg, Florida 33701, USA*

**Y. Rosenthal**

*Institute of Marine and Coastal Sciences, Department of Geology, Rutgers, State University of New Jersey, 71 Dudley Road, New Brunswick, New Jersey 08901, USA*

**A. Russell**

*Department of Geology, University of California, Davis, One Shields Avenue, Davis, California 95616, USA*

**T. Sagawa**

*Center for Advanced Marine Core Research, Kochi University, B200 Monobe, Nankoku, Kochi 783-8502, Japan*

**S. Sosdian**

*Institute of Marine and Coastal Sciences, Department of Geology, Rutgers, State University of New Jersey, 71 Dudley Road, New Brunswick, New Jersey 08901, USA*

**L. Stott**

*Department of Earth Sciences, University of South California, Los Angeles 90089, California, USA*

**K. Tachikawa**

*CEREGE, UMR UAMIII, CNRS, CDF, IRD, Europôle Méditerranéen de l'Arbois, BP 80, F-13545 Aix-en-Provence, France*

**E. Tappa and R. Thunell**

*Department of Geological Sciences, University of South Carolina, 701 Sumter Street, EWSC Room 617, Columbia, South Carolina 29208, USA*

**P. A. Wilson**

*National Oceanography Centre, European Way, Southampton SO14 3ZH, UK*

[1] An interlaboratory study of Mg/Ca and Sr/Ca ratios in three commercially available carbonate reference materials (BAM RS3, CMSI 1767, and ECRM 752-1) was performed with the participation of 25 laboratories that determine foraminiferal Mg/Ca ratios worldwide. These reference materials containing Mg/Ca in the range of foraminiferal calcite (0.8 mmol/mol to 6 mmol/mol) were circulated with a dissolution protocol for analysis. Participants were asked to make replicate dissolutions of the powdered samples and to analyze them using the instruments and calibration standards routinely used in their laboratories. Statistical analysis was performed in accordance with the International Standardization Organization standard 5725, which is based on the analysis of variance (ANOVA) technique. Repeatability ( $RSD_r\%$ ), an indicator of intralaboratory precision, for Mg/Ca determinations in solutions after centrifuging increased with decreasing Mg/Ca, ranging from 0.78% at Mg/Ca = 5.56 mmol/mol to 1.15% at Mg/Ca = 0.79 mmol/mol. Reproducibility ( $RSD_R\%$ ), an indicator of the interlaboratory method precision, for Mg/Ca determinations in centrifuged solutions was noticeably worse than repeatability, ranging from 4.5% at Mg/Ca = 5.56 mmol/mol to 8.7% at Mg/Ca = 0.79 mmol/mol. Results of this study show that interlaboratory variability is dominated by inconsistencies among instrument calibrations and highlight the need to improve interlaboratory compatibility. Additionally, the study confirmed the suitability of these solid standards as reference materials for foraminiferal Mg/Ca (and Sr/Ca) determinations, provided that appropriate procedures are adopted to minimize and to monitor possible contamination from silicate mineral phases.



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## 1. Introduction

[2] Reconstruction of past ocean temperatures from magnesium/calcium ratios in foraminiferal calcite has become an established technique during recent years [e.g., *Nurnberg et al.*, 1996; *Hastings et al.*, 1998; *Lea et al.*, 1999; *Mashiotta et al.*, 1999; *Elderfield and Ganssen*, 2000; *Rosenthal et al.*, 2000; *Dekens et al.*, 2002; *Anand et al.*, 2003]. Mg/Ca ratios in foraminiferal calcite are now measured routinely by different laboratories and comparability of results is an important issue.

[3] A consequence of the exponential relationship between Mg/Ca and temperature in foraminiferal calcite is that in order to ensure the accuracy of calculated temperatures, the relative measurement precision, expressed as a percentage of the measured ratio, must be maintained across the range of Mg/Ca ratios from low to high values. This is contrary to the usual situation in analytical methods [*Horwitz*, 1982], where relative measurement precision becomes worse with decreasing values. Increasing interest in temperatures calculated from the low Mg/Ca ratios found in benthic [*Billups and Schrag*, 2002, 2003; *Martin et al.*, 2002; *Marchitto and deMenocal*, 2003; *Lear et al.*, 2004; *Elderfield et al.*, 2006] and cold water planktonic foraminifera [*Pak et al.*, 2004; *von Langen et al.*, 2005; *Meland et al.*, 2006; *Nyland et al.*, 2006] further emphasizes the need for compatibility of Mg/Ca measurements between different laboratories.

[4] An interlaboratory comparison study conducted by *Rosenthal et al.* [2004] examined the reproducibility of Mg/Ca measurements within and between laboratories in foraminiferal calcite and in synthetic standard solutions. The study additionally included Sr/Ca because of the interest in studying secular variations in seawater Sr/Ca [*Martin et al.*, 1999; *Stoll et al.*, 1999; *Elderfield et al.*, 2000; *Shen et al.*, 2001] and growing potential for foraminiferal Sr/Ca thermometry in select genera

[*Mortyn et al.*, 2005]. Results showed that for the analyses of standard solutions, within laboratory instrumental precisions were usually better than 0.5% for measurements of both Mg/Ca and Sr/Ca, but interlaboratory precisions were significantly worse with relative standard deviations obtained of up to 3.4% for Mg/Ca and 1.8% for Sr/Ca. Among the conclusions of that interlaboratory study were the need for standards calibration among laboratories and the desirability of developing an agreed solid standard which could be used by laboratories in a manner analogous to the way reference standards are used in isotope analyses.

[5] The accuracy of standard solutions for element ratio determinations and the potential of commercially available carbonate reference materials for application to foraminiferal Mg/Ca (and Sr/Ca) determinations were investigated by *Greaves et al.* [2005]. These authors demonstrated that the errors involved in the preparation of instrument calibration standards for Mg/Ca and Sr/Ca determinations contribute significantly to interlaboratory analytical precision and proposed a limestone certified reference material (ECRM 752-1), containing Mg/Ca within the range of foraminiferal calcite (Mg/Ca = 3.75 mmol/mol), as a consistency standard which could be used within and between laboratories.

[6] Here we present the results of an interlaboratory study where three solid materials containing Mg/Ca in the range of foraminiferal calcite (0.8 mmol/mol to 6 mmol/mol) were analyzed by 25 participating laboratories. The advantage of circulating solid standards for intercalibration, rather than standard solutions, is that solid standards overcome the risk inherent in circulating small volumes of liquids that may not retain their initial compositions by the time they are analyzed. This must be balanced against stringent homogeneity and purity requirements for solid standards

**Table 1.** Certified Reference Materials

CRM	Certified by <sup>a</sup>	Quoted Element Concentrations (wt %)							
		Ca	Mg	Sr	Al	Fe	Mn	Si	Ti
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
BAM RS3	BAM	40.0	0.018	0.017	<0.001	<0.001	-	-	-

		Calculated Ratios (mmol/mol)							
	Material	Mg/Ca	Sr/Ca	Al/Ca	Fe/Ca	Mn/Ca	Si/Ca	Ti/Ca	
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	
BAM RS3	calcite	0.8	0.20	<0.02	<0.01	-	-	-	

<sup>a</sup>BAM, Bundesanstalt für Materialforschung und -prüfung, Germany; BAS, Bureau of Analysed Samples Ltd, Newnham Hall, Newby, Middlesborough, UK; CMSI, China Metallurgical Standardization Research Institute, Beijing.

[Greaves *et al.*, 2005]. Therefore, there were two objectives to the current study; first, compare instrumental standards calibrations between laboratories to assess within laboratory repeatability and between laboratory reproducibility; second, determine the suitability of the circulated solid standards as reference materials for foraminiferal Mg/Ca (and Sr/Ca) determinations.

## 2. Experimental Design

[7] This study followed the practice of previous interlaboratory studies [Rosell-Melé *et al.*, 2001; Rosenthal *et al.*, 2004] of maintaining anonymity by assigning random identification numbers to participating laboratories. Note that those numbers are different than the ones given for affiliations. The analytical scheme was constructed with reference to the International Union of Pure and Applied Chemistry (IUPAC) recommendations [Horwitz, 1994, 1995] for interlaboratory comparison studies. Samples of three solid standards were sent to each participant along with a dissolution protocol which participants were requested to follow, with the aim of minimizing effects that could result from different dissolution procedures and enabling the exercise to focus on instrument calibrations. Participants were asked to make replicate dissolutions on the powder samples and to analyze them using the instruments and calibration standards routinely used in their laboratory.

### 2.1. Standards

[8] Three potential solid standards for Mg/Ca determinations were identified from the list of commercially available carbonate reference materials compiled by Greaves *et al.* [2005]; BAM RS3,

a calcite CRM (Certified Reference Material) prepared by the Bundesanstalt für Materialforschung und -prüfung, Germany; CMSI 1767, a limestone CRM from the China Metallurgical Standardization Research Institute, Beijing; and ECRM 752-1, a limestone CRM issued by the Bureau of Analyzed Samples Ltd, UK previously examined by Greaves *et al.* [2005]. The materials were certified for Mg concentrations but not for Mg/Ca ratios at the precision, or sample sizes, relevant to foraminiferal Mg/Ca thermometry. Elemental concentrations taken from the certificates of analyses are listed in Table 1 together with calculated element/calcium ratios.

[9] Propagation of the quoted analytical errors on certified element concentrations gives errors (r.s.d.) on calculated Mg/Ca ratios of 2.7% (BAM RS3), 6.8% (ECRM 752-1) and 8.3% (CMSI 1767), insufficiently precise, with the possible exception of BAM RS3, to be directly relevant to foraminiferal Mg/Ca determinations. Foraminiferal calcite is composed of extremely pure (~99%) CaCO<sub>3</sub>, equivalent to 39.6% Ca, with four minor elements Na, Mg, Sr and F comprising most of the remainder [Lea, 1999] and the relative purity of these materials is shown by their calcium concentrations (Table 1). The presence of Al, Fe, Mn, Si and Ti is indicative of other mineral phases. Homogeneity of the solid materials and the contribution to measured Mg/Ca from the other mineral phases were investigated in preliminary studies before circulation.

### 2.2. Preliminary Studies

[10] Preliminary tests of homogeneity were performed on standards BAM RS3 and CMSI 1767 at Cambridge and LSCE, respectively, following the

**Table 2.** Average Mg/Ca Ratios Obtained for CMSI 1767 and BAM RS3 Standards Using Sample Weights in the Range 10–250 mg

	Sample Weights (mg)					
	10	20	50	100	250	10–250
<b>CMSI 1767 centrifuged</b>						
Mg/Ca (mmol/mol)	5.605	5.619	5.579	5.611	5.599	5.600
s.d.	0.029		0.006	0.02	0.002	0.019
r.s.d. (%)	0.51		0.10	0.35	0.04	0.35
n	2	1	3	3	2	11
<b>BAM RS3 centrifuged</b>						
Mg/Ca (mmol/mol)	0.802	-	0.789	0.798	0.793	0.796
s.d.	0.012	-	0.002	0.021	0.005	0.012
r.s.d. (%)	1.55	-	0.30	2.58	0.69	1.56
n	5	-	5	5	5	20
<b>CMSI 1767 not centrifuged</b>						
Mg/Ca (mmol/mol)	5.686	5.727	5.72	5.858	5.767	5.755
s.d.	0.025		0.011	0.156	0.016	0.096
r.s.d. (%)	0.45		0.20	2.67	0.28	1.67
n	3	1	3	3	2	12
<b>BAM RS3 not centrifuged</b>						
Mg/Ca (mmol/mol)	0.789	-	0.793	0.788	0.786	0.789
s.d.	0.004	-	0.004	0.002	0.003	0.004
r.s.d. (%)	0.47	-	0.46	0.02	0.44	0.51
n	5	-	5	5	5	20

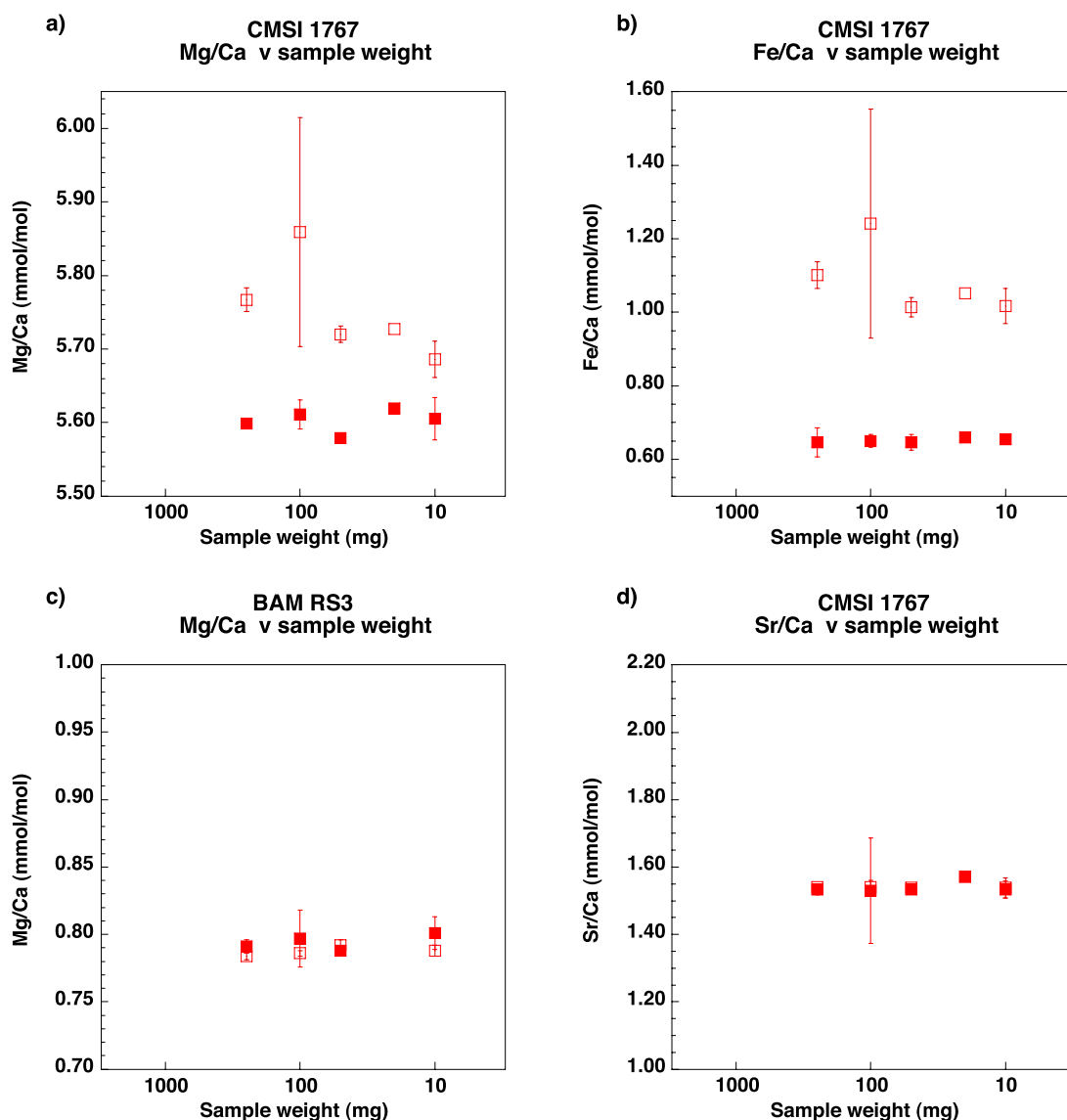
procedure used by *Greaves et al.* [2005] to test the homogeneity of ECRM 752-1. Replicate aliquots were taken from a single bottle of each standard for a series of weighings in the range 10 to 250 mg. Samples were dissolved in 0.075M HNO<sub>3</sub> in acid cleaned HDPE or LDPE bottles, using dissolution volumes in proportion to sample weights to give [Ca<sup>2+</sup>] of ~400 μg/g. Solutions were analyzed both with and without centrifugation; two 0.5 mL aliquots were taken, one centrifuged for 10 min at 9000 rpm then both diluted to [Ca<sup>2+</sup>] = 40 μg/g (CMSI 1767) or [Ca<sup>2+</sup>] = 100 μg/g (BAM RS3) and analyzed by ICP-OES. Mg/Ca results are reported in Table 2 and illustrated in Figure 1 which shows also Fe/Ca measurements in CMSI 1767.

[11] Results for CMSI 1767 (Figure 1a) demonstrate the contribution to Mg/Ca from insoluble noncarbonate minerals within this material which is confirmed by Fe/Ca (Figure 1b). Higher and more variable Mg/Ca and Fe/Ca in noncentrifuged samples, together with consistency between the Mg/Ca and Fe/Ca data sets in Figures 1a and 1b, show the effect of insoluble noncarbonate minerals on homogeneity of this material. Average Mg/Ca after centrifuging of 5.60 mmol/mol (0.019 s.d., 0.35% r.s.d on 11 measurements) confirms the within bottle homogeneity of the readily soluble carbonate material for samples in the 10 to 250 mg

weight range. Fe/Ca fell to consistent but nonzero values on centrifuging, with average Fe/Ca of 0.650 mmol/mol (0.018 s.d., 2.81% r.s.d on 11 measurements), again demonstrating homogeneity within the readily soluble carbonate matrix.

[12] In contrast, results for BAM RS3 (Figure 1c) show good agreement between centrifuged and noncentrifuged Mg/Ca measurements. Average Mg/Ca after centrifuging of 0.796 mmol/mol (0.012 s.d., 1.56% r.s.d) on 20 measurements was influenced by two high values. Omitting these gave Mg/Ca of 0.793 mmol/mol (0.008 s.d., 0.97% r.s.d) on 18 measurements, compared to noncentrifuged Mg/Ca of 0.789 mmol/mol (0.004 s.d., 0.51% r.s.d) on 20 measurements. Fe/Ca in BAM RS3 was consistently low and in most cases below detection, with a maximum of 0.004 mmol/mol observed. Slightly higher Mg/Ca ratios and the greater variability of centrifuged compared to noncentrifuged samples may be a consequence of the additional handling involved and effect of the associated analytical blank on the low Mg/Ca of this material.

[13] Measurements of Sr/Ca in CMSI 1767 (Figure 1d) revealed a ratio comparable to Sr/Ca in foraminiferal calcite and good homogeneity within this material from measurements both with and without centrifugation. Average Sr/Ca for samples in the 10 to 250 mg weight range was 1.542 mmol/mol (0.010 s.d., 0.66% r.s.d) on 11



**Figure 1.** Homogeneity of CMSI 1767 and BAM RS3, measured element ratio versus sample weight: (a) CMSI 1767 Mg/Ca; (b) CMSI 1767 Fe/Ca; (c) BAM RS3 Mg/Ca; and (d) CMSI 1767 Sr/Ca. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution.

measurements after centrifuging and 1.536 mmol/mol (0.013 s.d., 0.86% r.s.d) on 11 measurements without centrifuging.

[14] The results of the preliminary studies confirmed homogeneity within the carbonate mineral phases of both materials over the range of sample weights used. Mg/Ca in CMSI 1767 showed a relationship to Fe/Ca similar to that observed previously for ECRM 752-1 by Greaves *et al.* [2005], consistent with the quoted concentrations and calculated ratios shown in Table 1. The similar Sr/Ca ratio to foraminiferal calcite found in CMSI 1767 was an added bonus of this material.

### 2.3. Sample Preparation and Distribution

[15] All samples were prepared at LSCE from previously unopened bottles of the standards, containing 80 g CMSI 1767 (without lot number), 100 g BAM RS3 (lot number 41), 100 g ECRM 752-1 (lot number 2133). The standards were mixed well in case of settling during storage then, following the homogeneity tests detailed in the previous section, one gram portions of each standard were weighed into a series of glass sample bottles precleaned by soaking for 24 hours in 10% HNO<sub>3</sub>, rinsed with high-purity water and dried for 24 hours. Thus, for each standard, all samples sent

to laboratories came from the same initial bottle on which homogeneity had been verified.

[16] The participating laboratories were each sent one subsample bottle of each of the three standards and requested to perform replicate analyses as described in section 2.4 except that as a check on homogeneity of the materials after subsampling, one laboratory (25) was sent five subsample bottles of each standard and asked to make a single determination from each subsample.

## 2.4. Protocol for Dissolution

[17] The primary objective of this Mg/Ca interlaboratory comparison was to check instrumental calibrations between laboratories and a dissolution protocol was devised with the aim of minimizing effects from noncarbonate mineral phases in the standards and from laboratories following different procedures. Participants were requested to follow the following procedure: (1) number of replicate dissolutions, 6 per standard; (2) sample weight, 50 mg; (3) dissolution volume, 50 mL; (4) dissolution acid, 0.075M HNO<sub>3</sub> (or as routinely used in their laboratory); (5) samples to be dissolved and analyzed on the same day; (6) a blank solution to be included; (7) solutions to be analyzed both with and without centrifuging, and (8) samples to be diluted as required for the usual instrumental procedures of each laboratory.

[18] It was intended that after initial bottle cleaning and reagent preparation, the dissolution and analyses could be completed in a single day of laboratory and instrument time. Laboratories performing analyses in solution were asked to follow, as far as possible, the protocol supplied. Laboratories doing analyses not in solution were free to investigate the materials as they saw fit. In addition to results for Mg/Ca, participants were asked to provide data for Sr/Ca and for elements indicating silicate contamination, such as Al, Fe, Mn, Si, Ti, depending on those typically measured in their laboratory. The participants were provided with the approximate Mg/Ca ratios of the three materials calculated from quoted element concentrations (Table 1), but were not informed of the Sr/Ca ratio found for CMSI 1767 in the preliminary studies, making CMSI 1767 a blind sample for the determination of Sr/Ca.

## 2.5. Reporting of the Results

[19] A file containing spreadsheets for returning experimental information and results using a template for each material was sent with the protocol.

On return the files were first screened to ensure that no laboratory or personal information had been included and that results were identified only by laboratory numbers before being passed to the coordinators. In this way anonymity was preserved both among participants and the coordinators when examining data. The results were tabulated in a common format by the coordinators to give a single value for each sample of material dissolved and analyzed before calculating the mean of replicate analyses by each laboratory, i.e., where some laboratories had made multiple determinations on a single dissolution of material these were combined to give a single result per analysis. The complete set of results, individual analyses, means and standard deviations of replicate dissolutions by each laboratory are presented in auxiliary material<sup>1</sup> Tables S1–S3. Statistical analysis of the data followed the protocol of *Horwitz* [1995] and the guidelines of *AOAC International* [2006]. One of the criteria specified in this protocol is that only valid data should be subject to statistical analysis. In the context of this exercise, valid Mg/Ca data are those where significant influences from other noncarbonate phases can be excluded and therefore, results for each of the three materials were examined critically, as described in section 3, to identify nonvalid data on analytical grounds as preferable to relying on statistical tests alone [*Horwitz*, 1995].

## 2.6. Outlier Testing

[20] The outcome of outlier tests depends to a large extent on the tests themselves and how they are applied. Statistical tests can identify observations which differ from the majority of others according to the rules applied, but cannot give a reason. A decision to label data as outliers should reflect scientific experience as much as the application of a statistical rule [*Horwitz*, 1995; *Davies*, 1988; *Meier and Zünd*, 2000]. The following tests were applied with these caveats in mind.

[21] Measurements identified as outliers for analytical reasons by individual laboratories were first excluded, then a three-sigma test (three standard deviation test) was applied to each set of data for a standard and laboratory. Data superior to the mean plus 3 sigma, or inferior to the mean minus 3 sigma, were excluded and means recalculated before data were submitted to outlier testing using Cochran and Grubbs tests [*Horwitz*, 1995; *AOAC International*, 2006]. The Cochran test is used to

<sup>1</sup>Auxiliary materials are available at <ftp://ftp.agu.org/apend/gc/2008GC001974>.



identify sets of results showing significantly greater variability among replicate (within-laboratory) analyses than the other laboratories for a given material. This test was applied as a 1-tail test at a probability value of 2.5%. To apply this test, we computed the within-laboratory variance for each laboratory and divided the largest of these by the sum of the variances. The resulting quotient is the Cochran statistic which indicates the presence of a removable outlier if the critical value listed in the Cochran table for  $P = 2.5\%$  is exceeded. The Grubbs test is used to identify laboratories with extreme averages. This test was applied in the following order: single value test (2-tail;  $P = 2.5\%$ ); then if no outlier was found a pair value test was applied (2 values at the highest end and 2 values at the lowest end; then 2 values, one at each end, at an overall  $P = 2.5\%$ ).

### 2.7. Statistical Data Treatment

[22] To perform statistical data treatment, we followed the *International Standardization Organization* [1994], which is based on the analysis of variance (ANOVA) method. We applied a statistical scheme equivalent to that commonly used in interlaboratory analytical studies [Nilsson *et al.*, 1997; Rosell-Melé *et al.*, 2001; Rosenthal *et al.*, 2004]. Summary statistics ( $S_r$ ,  $S_R$ ,  $RSD_r$ ,  $RSD_R$ ) were calculated for the average ratios and overall method precisions for each of the three standards. In this scheme, we focused on: the single-analyst standard deviation ( $S_r$ , repeatability), the precision associated with the performance of an individual laboratory, the overall standard deviation ( $S_R$ , reproducibility), the precision associated with measurements generated by a group of laboratories. The repeatability  $RSD_r$  is determined from the repeatability standard deviation ( $S_r$ ) and the average concentration for a particular test sample, giving an indication of the intralaboratory precision. The reproducibility  $RSD_R$ , determined from the reproducibility standard deviation ( $S_R$ ) and the average concentration of a particular test sample, gives an indication of the interlaboratory method precision. Equating  $S_R$  to measurement uncertainty and assuming a normal distribution gives a confidence interval of  $\sim 67\%$  that the result plus and minus  $S_R$  will encompass the “true” value. Multiplying  $S_R$  by a coverage factor of 2 gives the “expanded measurement uncertainty” with a confidence interval of  $\sim 95\%$  that the result plus and minus  $2S_R$  will encompass the “true” value. The reproducibility limit (R) or repeatability limit (r) is the value less than or equal to which the absolute difference

between two results obtained under reproducibility or repeatability conditions is expected to be with a probability of 95%. For a normal distribution  $r = 2.8S_r$  and  $R = 2.8S_R$ .

## 3. Results and Discussion

[23] The twenty-five participating laboratories each returned results of Mg/Ca determinations on one or more of the three materials, twenty-four laboratories performed analyses after dissolution and one used a flow through method [Benway *et al.*, 2003]. Instrumental determinations were by either inductively coupled plasma optical emission spectrophotometry (ICP-OES), used by sixteen laboratories or inductively coupled plasma mass spectrometry (ICP-MS), by nine laboratories. The supplied experimental protocol was followed by most of the participants although four laboratories used significantly smaller quantities of solid material (10–20 mg) than the 50 mg proposed. Homogeneity implications of using small samples are assessed during discussion of the results. Twenty-two laboratories returned results of Sr/Ca determinations in addition to Mg/Ca. Element ratios frequently used as contamination indicators [e.g., Barker *et al.*, 2003; Lea *et al.*, 2005] were returned by the laboratories as follows; Mn/Ca by thirteen laboratories, Fe/Ca by eight, Al/Ca by seven, Ti/Ca by five and Si/Ca by two laboratories. Data for other trace element ratios including Ba/Ca, Cd/Ca, Nd/Ca, U/Ca and Zn/Ca were returned by one laboratory or more with a maximum of five participants returning results of Ba/Ca determinations. Details of the procedures used and number of results reported for each material and element ratio measured are given in auxiliary material Tables S1–S3.

[24] Results for Mg/Ca, Sr/Ca and element ratios measured to indicate possible contamination from noncarbonate phases are presented and discussed for each of the three materials separately in sections 3.1 to 3.3. Comparisons between the three materials are made in section 3.4. Analytical details, individual results, means and statistics are presented in detail for each material in auxiliary material Tables S1–S3. Results for other trace metal ratios which do not relate directly to Mg/Ca are included in auxiliary material Tables S1–S3.

### 3.1. BAM RS3

[25] Mg/Ca was determined in BAM RS3 by all twenty-five participants on samples without centrifugation and by twenty-one laboratories after centri-

fuging solutions. Results are shown in Table 3 and mean values plotted for each laboratory in Figure 2, in ascending order of uncentrifuged values, using data before statistical rejection. A single data point, flagged as contaminated by a laboratory (25) was excluded from results after centrifugation. Error bars plotted in Figure 2 are  $\pm 2$  standard errors on the mean ( $= 2 \cdot \text{SD} / \sqrt{n}$ ) to allow for the different number of determinations by laboratories. Histograms of the individual measurements, for solutions after centrifuging, are presented in Figure 3, showing the distribution of results among laboratories (Figure 3a) and comparing results obtained by the two instrumental techniques (Figure 3b).

[26] Within laboratory standard deviations, including all results except the determination identified as contaminated, average 0.010 mmol/mol (centrifuged) and 0.013 mmol/mol (not centrifuged) which, because of the low Mg/Ca in this material, translate into average intralaboratory precisions of 1.33% and 1.64%, respectively. The average precisions conceal a wide range in intralaboratory repeatability, from 0.17% to 4.31% for determinations after centrifuging and 0.12% to 7.58% (or 5.95% excluding the flow through technique, lab 29), for determinations without centrifuging (Table 3).

[27] Between laboratory precisions, again taking all results for Mg/Ca determinations in BAM RS3, are approximately four times worse than average within laboratory precisions at 5.4% and 5.6% for centrifuged and not centrifuged results, respectively. With the exception of laboratory 18 and to a lesser extent laboratories 3 and 19, the results with and without centrifuging are in agreement, giving overall mean Mg/Ca, before statistical analysis, from all laboratories of 0.775 mmol/mol (0.043 s.d., 5.57% r.s.d) on 25 determinations without centrifuging and 0.784 mmol/mol (0.043 s.d., 5.44% r.s.d) on 21 determinations after centrifuging (Table 3).

[28] The range of the results shown in Figures 2 and 3 could be caused by a number of analytical or geochemical factors and these are investigated here before discussing statistical analysis of the data. Three laboratories (13, 17, 26) used small (10 mg) samples for dissolution. Laboratory 13 performed analyses without centrifugation only but results of centrifuged and not centrifuged determinations from laboratories 17 and 26 are in close agreement, suggesting that homogeneity of the solid material when using 10 mg is not a major factor, in

agreement with the preliminary homogeneity study described in section 2.2. If results for these laboratories, and also lab 29 which used the flow through procedure, are omitted, the between laboratory reproducibility is improved slightly but with little effect on the mean values obtained (Table 3), simply because results from laboratories 17 and 26 were above average, while those from laboratories 29 and 13 were below.

[29] The potential for magnesium contamination in analyses of BAM RS3 is significant because of its low Mg/Ca ratio. The dissolution protocol was designed to minimize the effect of the Mg blank during dissolution by producing high initial concentrations. Most laboratories adhered to this (Table 3) with a minimum initial Ca concentration, used by laboratory 13, of 120  $\mu\text{g/g}$ . Calcium concentrations of the final instrumental determinations cover a very wide range from 1 to  $>400 \mu\text{g/g}$ , some laboratories diluting solutions before running while others ran concentrates without dilution. Although the possibility of Mg contamination can never be excluded and it may contribute to within laboratory repeatability, there is no apparent relationship between the concentrations used for final determination (Table 3) and the Mg/Ca results shown in Figure 2.

[30] Laboratories where other element ratios were determined, including Al/Ca, Fe/Ca, Mn/Ca, Si/Ca, Ti/Ca, as indicators of contamination by noncarbonate minerals found very low values in BAM RS3, confirming the results of the preliminary study and anticipated from the quoted element concentrations shown in Table 1. Similarly, Sr/Ca in this material was confirmed to be very low at approximately 0.18 mmol/mol, from both centrifuged and noncentrifuged determinations, much lower than relevant to the typical Sr/Ca range of 1.0–1.5 mmol/mol found in foraminiferal calcite. Results are included in the auxiliary material.

[31] Statistical analysis using the Cochran test rejects results from laboratories 19, 29 and 33 for analyses without centrifuging, and from laboratories 6, 18 and 22 (and 29) for analyses after centrifuging, on the basis of the within laboratory variance (Table 3 and Figure 2). After exclusion of results identified by the Cochran test, no outlying average values were found on application of the Grubbs test. The results after statistical data rejection are Mg/Ca = 0.791 mmol/mol (0.030 s.d., 3.79% r.s.d) on 18 determinations after centrifuging and Mg/Ca = 0.777 mmol/mol (0.043 s.d., 5.53% r.s.d) on 22 determinations without centri-

**Table 3.** Results From Each Laboratory for the Determination of Mg/Ca in BAM RS3

Lab ID	Dissolution		Centrifuged Solutions						Not Centrifuged						
	Wt Solid (mg)	Volume (mL)	[Ca] ( $\mu\text{g/g}$ )	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n
1	50	40	500	100	0.801	0.010	1.24	0.008	6	100	0.800	0.012	1.45	0.010	6
2	50	50	400							430	0.785	0.012	1.56	0.010	6
3	50	50	400	360	0.813	0.005	0.63	0.004	6	400	0.842	0.004	0.49	0.003	6
4	20–50	20–50	400	40	0.770	0.011	1.37	0.009	6	40	0.765	0.008	1.01	0.006	6
5	50	50	400	50	0.804	0.017	2.10	0.015	5	50	0.814	0.018	2.16	0.016	5
6	50	50	400	20	0.747	0.022	2.95	0.018	6	20	0.743	0.008	1.12	0.007	6
7	50	50	400							40	0.751	0.005	0.66	0.004	6
12	50	50	400	40	0.782	0.003	0.40	0.003	6	40	0.774	0.005	0.65	0.004	6
13	10	35	120							120	0.738	0.002	0.24	0.001	6
14	50	50	400	160	0.777	0.004	0.48	0.003	6	160	0.780	0.005	0.67	0.004	6
16	50	50	400	80	0.792	0.017	2.09	0.014	6	80	0.790	0.007	0.89	0.006	6
17	10	10	400	80	0.848	0.004	0.45	0.003	6	80	0.847	0.007	0.88	0.006	6
18	50	50	400	50	0.834	0.036	4.31	0.029	6	50	0.726	0.007	1.01	0.006	6
19	50	50	400	60	0.798	0.011	1.42	0.009	6	60	0.775	0.038	4.88	0.031	6
20	50	50	400	70	0.824	0.001	0.17	0.002	3	70	0.823	0.001	0.12	0.001	6
21	50	50	400	80	0.787	0.004	0.49	0.003	6	80	0.787	0.008	0.98	0.006	6
22	50	50	400	50	0.656	0.023	3.53	0.019	6	50	0.671	0.008	1.20	0.007	6
23	50	50	400	20	0.741	0.007	1.00	0.006	6	20	0.749	0.009	1.21	0.007	6
24	50	50	400	4	0.810	0.005	0.57	0.004	6	4	0.809	0.011	1.34	0.009	6
25	50	50	400	100	0.784	0.002	0.24	0.002	4	100	0.783	0.003	0.44	0.003	5
26	10	5	800	160	0.823	0.004	0.47	0.003	6	160	0.832	0.012	1.42	0.010	6
29											0.705	0.053	7.58	0.062	3
30	50	50	400	100	0.725	0.007	0.93	0.007	4	100	0.726	0.015	2.04	0.012	6
31	40–68	50	330–530	50	0.757	0.009	1.17	0.007	6	50	0.756	0.008	1.12	0.007	6
33	50	50	400	1	0.800	0.016	1.94	0.013	6	1	0.807	0.048	5.95	0.039	6
All results															
Mean (mmol/mol)					0.784	0.010	1.33	0.009			0.775	0.013	1.64	0.011	
s.d.					0.043						0.043				
r.s.d. (%)					5.44						5.57				
n					21						25				
>10 mg powder															
Mean					0.779	0.011	1.42	0.009			0.774	0.011	1.47	0.009	
s.d.					0.041						0.039				
r.s.d. (%)					5.28						5.01				
n					19						21				
After statistical analysis for outliers															
Mean					0.791	0.008	0.95	0.006			0.777	0.008	1.03	0.007	
s.d.					0.030						0.043				
r.s.d. (%)					3.79						5.53				
n					18						22				

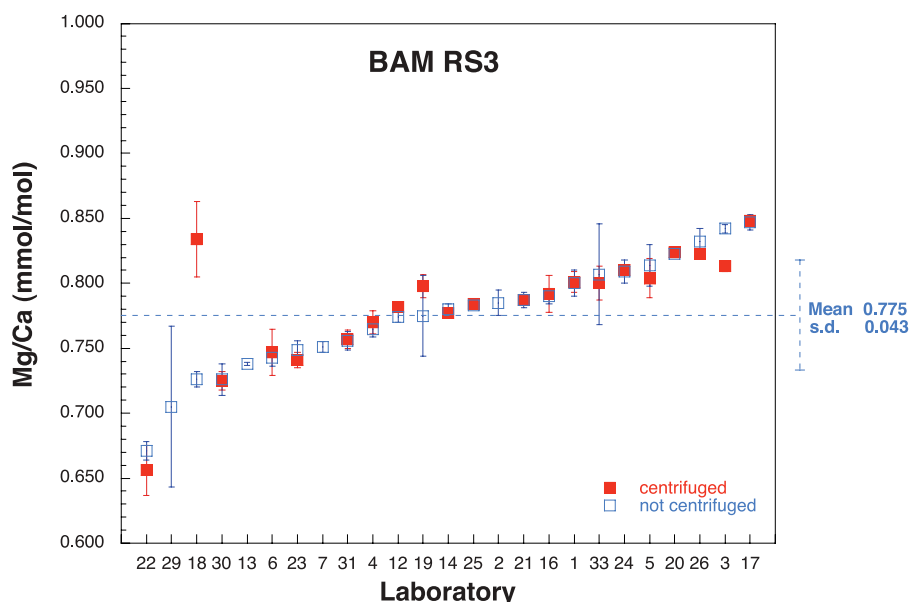
fusing (Table 3). Following statistical data rejection, results obtained by ICPMS are indistinguishable from those obtained by ICP-OES (Figure 3b), in agreement with the conclusions of a recent study [Andreasen *et al.*, 2006].

[32] The mean values obtained from both noncentrifuged and centrifuged determinations, either with or without statistical data rejection, are close to the Mg/Ca ratio of 0.8 mmol/mol calculated from the certified concentrations (Table 1). The material circulated showed good homogeneity and purity and is a valuable reference material for Mg/Ca

determinations. However, the spread of results shown in Figure 2 and the associated reproducibility statistics highlight the discrepancy between calibration standards used by laboratories. Results of the analysis of variance (ANOVA) are presented and discussed with those from the other two materials in section 3.4.

### 3.2. ECRM 752-1

[33] Results for Mg/Ca in ECRM 752-1 are presented in Table 4. Twenty-four laboratories analyzed the material without centrifugation and



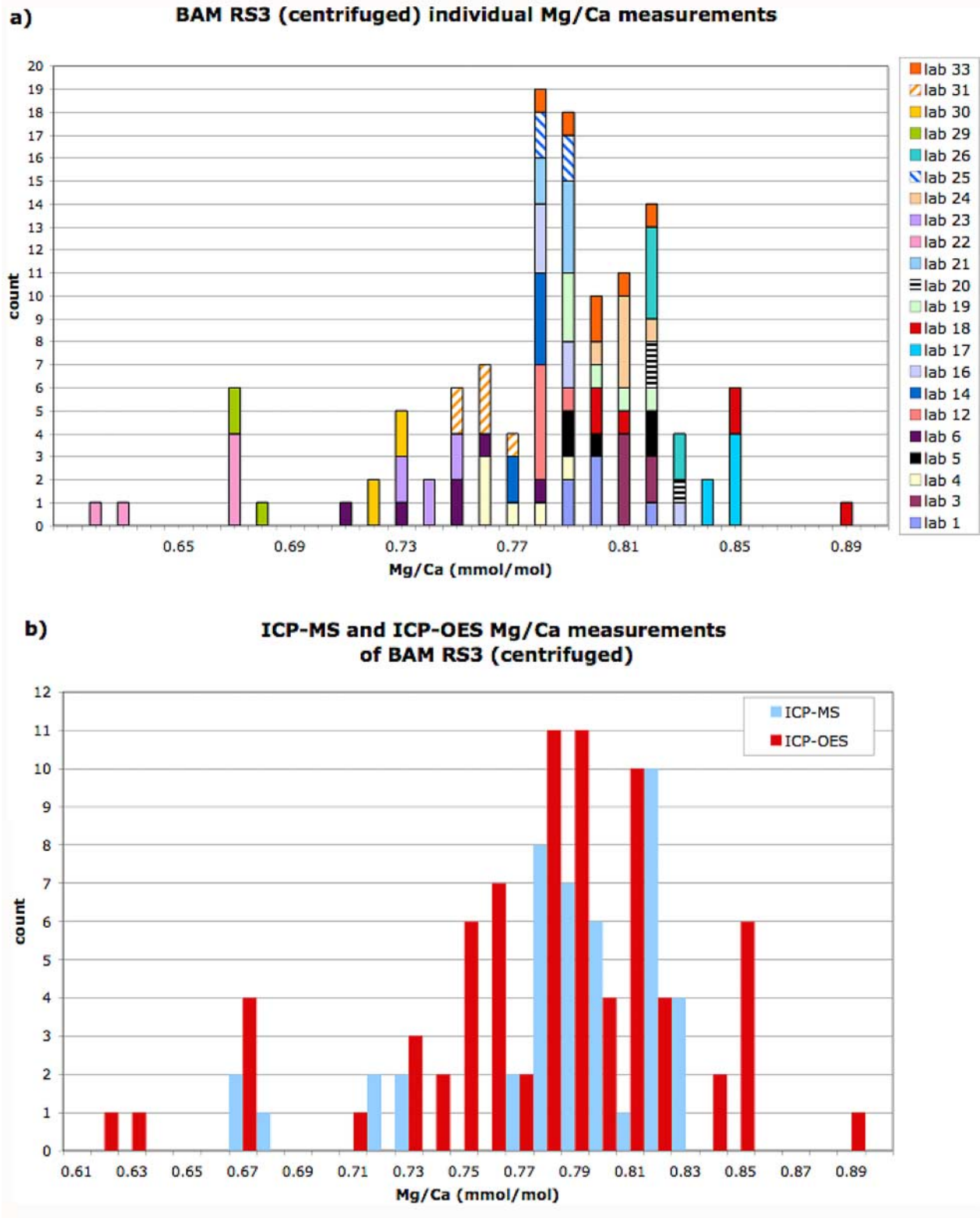
**Figure 2.** BAM RS3. Mg/Ca means of results from each laboratory, without statistical rejection. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution. Error bars are  $\pm 2$  std errors on the mean from each laboratory. Interlaboratory mean and standard deviation before statistical rejection shown for not centrifuged analyses.

twenty-one laboratories after centrifuging solutions. The means were calculated using all data submitted by the participants except for one data point flagged as an outlier in results after centrifugation by the participating laboratory (24) and one data point excluded from results before centrifugation (Lab 5) on the basis that it was more than three standard deviations from the mean. The complete data set is presented in auxiliary material Tables S1–S3. Mean values obtained by each laboratory for this material are plotted in Figure 4a in ascending order of centrifuged values and individual measurements are shown in histograms in Figures 5a and 5b.

[34] Within laboratory standard deviations were similar for analyses both with and without centrifuging, averaging 0.026 and 0.027 mmol/mol, respectively, and equivalent to within laboratory precisions of 0.70% r.s.d. for this material. As found for BAM RS3, within laboratory precisions cover a wide range, from 0.18 to 1.47% for determinations after centrifuging solutions and 0.16 to 2.31% for determinations without centrifuging (Table 4). The between laboratory precisions are approximately 3.5 times worse than within laboratory precision, again reflecting the situation found for BAM RS3.

[35] It was demonstrated previously [Greaves *et al.*, 2005] that silicate mineral phases within this material must be removed in order to obtain

reproducible Mg/Ca results from the carbonate. Eight laboratories measured Fe/Ca as an indicator of silicate contamination (Figure 4b) and seven measured Al/Ca (Figure 4c). Fewer participants determined Si/Ca or Ti/Ca while thirteen laboratories returned Mn/Ca measurements. The results are included in the complete data set in auxiliary material Tables S1–S3. The effect of silicate contamination on noncentrifuged Mg/Ca determinations is evident in Figure 4a and confirmed, where available, by Fe/Ca and Al/Ca (Figures 4b and 4c). Fe/Ca falls to approximately 0.07 mmol/mol on centrifuging and Al/Ca to  $< 0.3$  mmol/mol, below or very close to detection by ICP-OES. Where laboratories did not determine either Fe/Ca or Al/Ca it must be assumed that the centrifugation procedure used was adequate to remove any suspended undissolved silicate minerals. ICP-MS results for Al/Ca were returned by laboratory 29 using the flow through method [Benway *et al.*, 2003] where a mean Al/Ca of 0.17 mmol/mol was found. This is close to the average Al/Ca of 0.13 mmol/mol returned by three laboratories after centrifugation (Figure 4c) and, except for one determination (Lab 20), much lower than the average Al/Ca of 0.65 mmol/mol found without centrifugation. It would appear from this evidence to be appropriate to include results by the flow through method with centrifuged rather than non-centrifuged data.



**Figure 3.** BAM RS3. Histograms of Mg/Ca results from each laboratory for solutions after centrifuging: (a) individual measurements from each laboratory and (b) comparison of results by ICP-MS and ICP-OES.

**Table 4.** Results From Each Laboratory for the Determination of Mg/Ca in ECRM 752-1

Lab ID	Dissolution		Centrifuged Solutions						Not Centrifuged						
	Wt Solid (mg)	Volume (mL)	[Ca] ( $\mu\text{g/g}$ )	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n
1	50	40	500	100	3.677	0.032	0.87	0.026	6						
2	50	50	400	400						430	3.983	0.029	0.72	0.023	6
3	50	50	400	400	3.818	0.013	0.35	0.011	6	400	4.013	0.023	0.58	0.019	6
4	23	23	400	40	3.718	0.017	0.45	0.019	3	40	3.790	0.010	0.25	0.011	3
5	50	50	400	50	3.761	0.044	1.18	0.036	6	50	3.796	0.033	0.86	0.029	5
6	55	55	400	20	3.828	0.036	0.95	0.030	6	20	3.807	0.018	0.47	0.015	6
7	50	50	400	40						40	3.799	0.013	0.35	0.011	6
12	50	50	400	40	3.746	0.011	0.30	0.009	6	40	3.807	0.009	0.23	0.007	6
13	10	40	120	120						120	4.027	0.022	0.54	0.018	6
14	50	50	400	160	3.789	0.011	0.30	0.009	6	160	3.774	0.020	0.53	0.016	6
16	50	50	400	80	3.749	0.015	0.40	0.012	6	80	3.802	0.016	0.41	0.013	6
17	10	10	400	80	3.867	0.016	0.42	0.013	6	80	3.919	0.024	0.62	0.020	6
18	50	50	400	50	3.791	0.026	0.67	0.021	6	50	3.786	0.054	1.44	0.044	6
19	50	50	400	60	3.504	0.038	1.09	0.031	6	60	3.747	0.052	1.39	0.042	6
20	50	50	400	70	3.755	0.046	1.23	0.046	4	70	3.809	0.020	0.52	0.016	6
21	50	50	400	80	3.783	0.007	0.19	0.006	6	80	3.870	0.006	0.16	0.005	6
22	50	50	400	40	3.676	0.054	1.47	0.044	6	40	3.714	0.027	0.73	0.022	6
23	50	50	400	20	3.797	0.042	1.10	0.034	6	20	3.875	0.044	1.15	0.036	6
24	50	50	400	4	3.883	0.014	0.37	0.013	5	4	3.941	0.008	0.19	0.006	6
25	50	50	400	100	3.736	0.013	0.35	0.012	5	100	3.775	0.007	0.19	0.007	5
26	10	5	800	160	3.727	0.019	0.51	0.016	6	160	3.697	0.009	0.25	0.008	6
29											3.727	0.055	1.48	0.064	3
30	50	50	400	100	3.861	0.039	1.01	0.032	6	100	3.832	0.045	1.18	0.037	6
31	50	50	400	50	3.617	0.007	0.18	0.005	6	50	3.674	0.008	0.21	0.006	6
33	50	50	400	1	3.677	0.050	1.35	0.041	6	1	3.806	0.088	2.31	0.072	6
All results (not including 29 with centrifuged)															
Mean (mmol/mol)					3.750	0.026	0.70	0.022		3.824	0.027	0.70	0.023		
s.d.					0.089					0.095					
r.s.d. (%)					2.36					2.48					
n					21					24					
>10 mg powder															
Mean					3.746	0.027	0.73	0.023		3.820	0.026	0.69	0.022		
s.d.					0.089					0.083					
r.s.d. (%)					2.38					2.17					
n					19					20					
Including Lab 29															
Mean					3.749	0.026	0.69	0.023							
s.d.					0.087										
r.s.d. (%)					2.31										
n					22										
Excluding Lab 19															
Mean					3.761	0.027	0.72	0.024							
s.d.					0.069										
r.s.d. (%)					1.83										
n					21										

[36] Most of the participating laboratories used the 50 mg sample size requested in the dissolution protocol but smaller samples of 23 mg (Lab 4) and 10 mg (Labs 13, 17 and 26) were also used. Exclusion of results from these laboratories had little effect on the mean values and reproducibility (Table 4), confirming the homogeneity of ECRM

752-1 for sample sizes of 10 mg and above when solutions are analyzed after centrifuging [Greaves *et al.*, 2005].

[37] Mn/Ca ratios were similar from both centrifuged and noncentrifuged determinations, with Mn/Ca = 0.132 mmol/mol (0.009 s.d. 6.6% r.s.d)

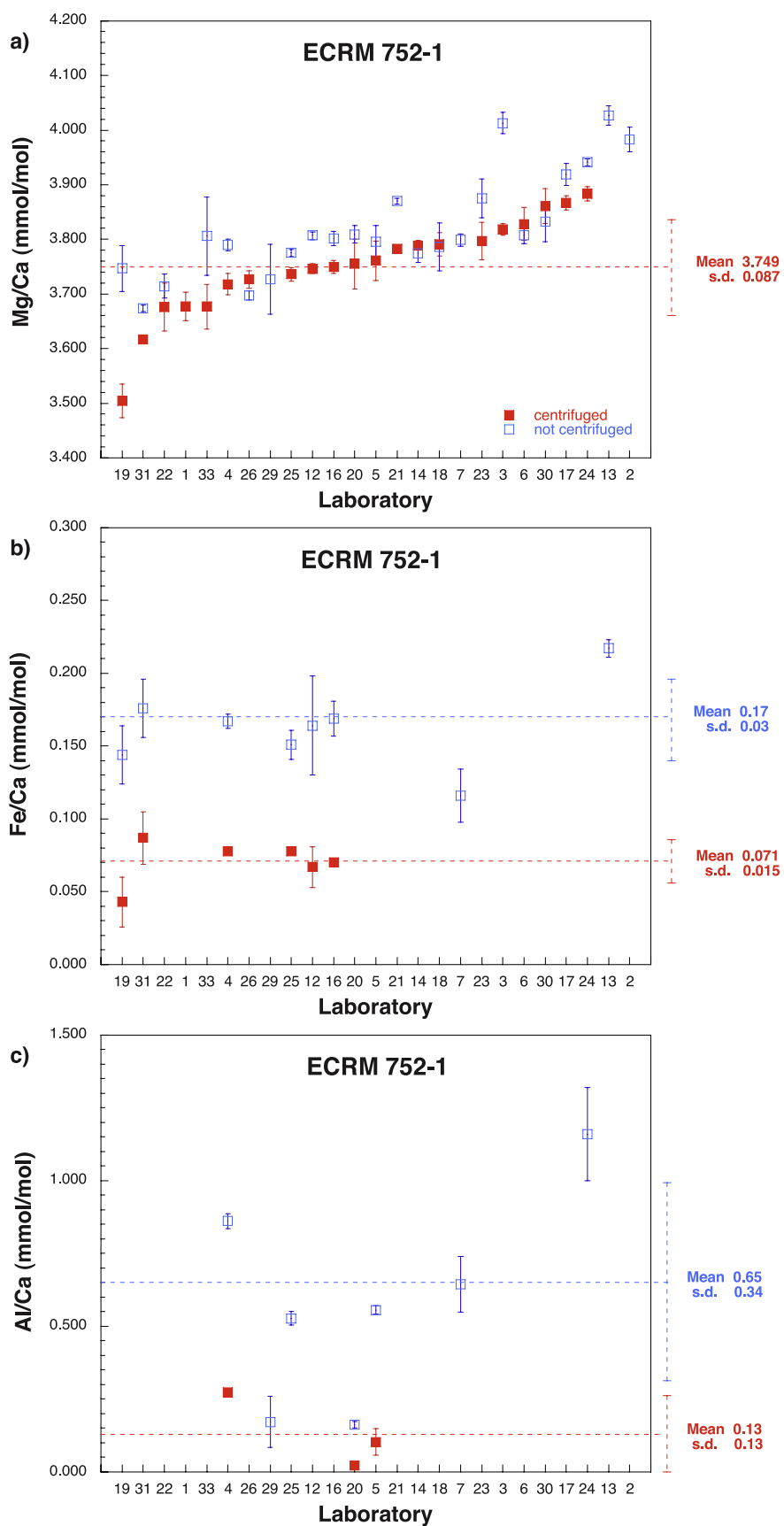


Figure 4

on determinations by 13 laboratories without centrifuging and  $Mn/Ca = 0.132$  mmol/mol (0.008 s.d. 6.3% r.s.d) on determinations by 12 laboratories after centrifuging. The low Sr/Ca ratio in ECRM 752-1 calculated from quoted element concentrations (Table 1), reported previously [Greaves *et al.*, 2005], was confirmed by the 21 laboratories that returned results for Sr/Ca.

[38] Statistical analysis of the results for Mg/Ca determinations after centrifuging identified no outliers, either on the basis of high within laboratory variance (Cochran test) or extreme average values (Grubbs test), the lowest Mg/Ca mean value (Figure 4a, Lab 19) falling just within the critical value of the Grubbs extreme deviation outlier test. Including results obtained using the flow through method, a mean measured Mg/Ca = 3.749 mmol/mol (0.087 s.d., 2.31% r.s.d) was obtained on 22 determinations after centrifuging (Table 4). If the results after centrifuging from Lab 19 are excluded (see discussion in section 3.4) then mean Mg/Ca = 3.761 mmol/mol (0.069 s.d., 1.87% r.s.d) on 21 determinations (Table 4). As found for BAM RS3, results obtained by ICPMS are statistically indistinguishable from those obtained by ICP-OES (Figure 5b).

### 3.3. CMSI 1767

[39] CMSI 1767 has the highest Mg/Ca ratio of the three materials circulated and contains the largest contribution from noncarbonate minerals, as shown in Table 1 and confirmed by the preliminary homogeneity study (Figure 1). Mg/Ca was determined in this material by twenty-four laboratories without centrifugation and twenty-two laboratories on solutions after centrifuging. The results of Mg/Ca determinations in CMSI 1767 are shown in Table 5, calculated using all results with the exception of four data points. Two data points were flagged as outliers by the three sigma test in results after centrifuging; one from Lab 5, one from Lab 19, and two identified as outliers in results without centrifugation; one from Lab 16 and one from Lab 4 where anomalously high Mg/Ca was associated with high Al/Ca, Fe/Ca and Ti/

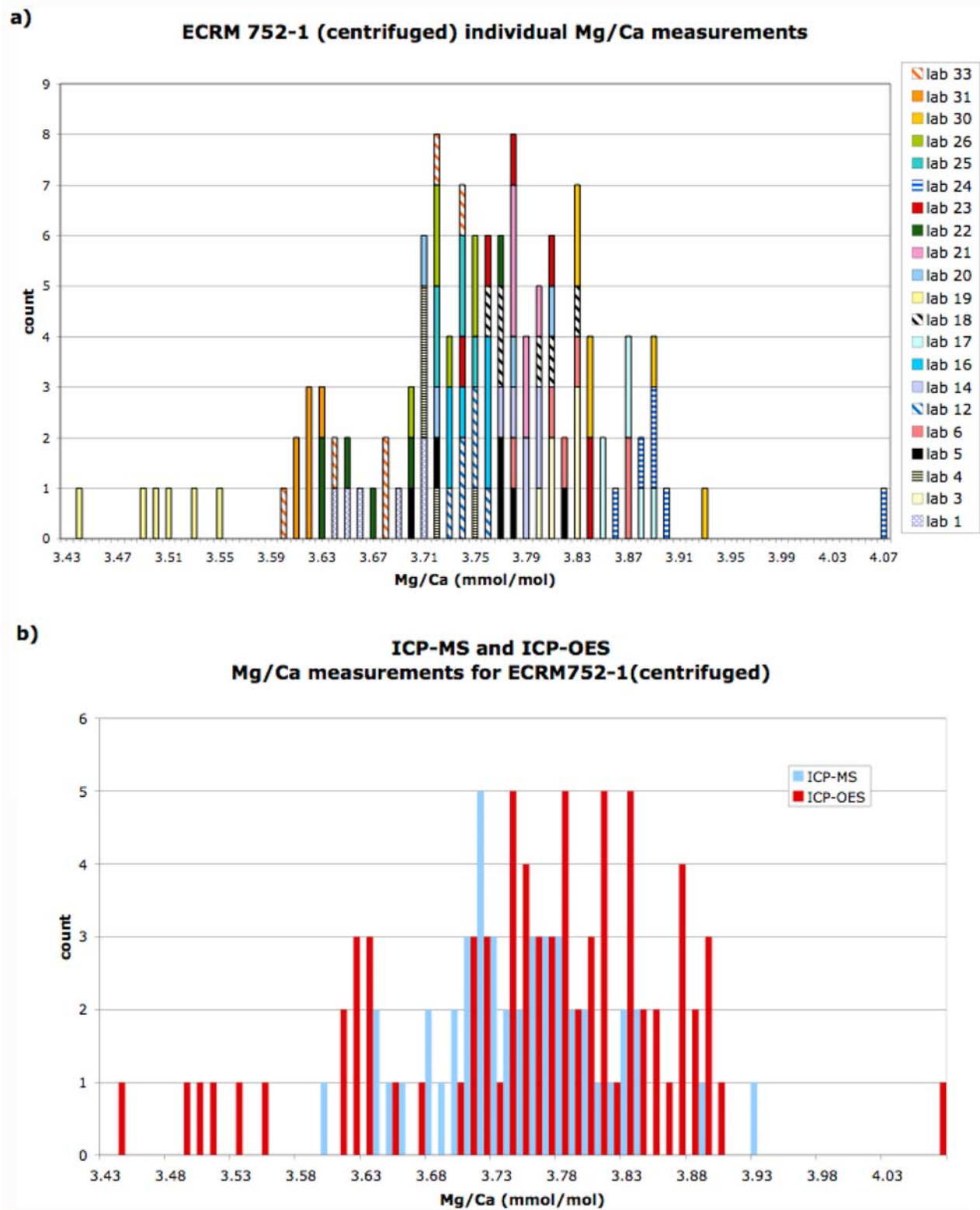
Ca. The complete data set is included in auxiliary material Tables S1–S3. Mean Mg/Ca ratios obtained by each laboratory are plotted in Figure 6a in ascending order of centrifuged values and individual measurements for Mg/Ca determinations in solutions after centrifuging are shown in histograms in Figures 7a and 7b.

[40] Average within laboratory standard deviations for analyses of this material both with and without centrifuging were similar at 0.040 and 0.047 mmol/mol, respectively, equivalent to within laboratory precisions of 0.71% and 0.82% r.s.d. Again, the average within laboratory precisions masked a wide range between individual laboratories, from 0.24 to 1.69% for determinations after centrifuging solutions and 0.17 to 1.88% for determinations without centrifuging (Table 5). The between laboratory precisions were approximately three times worse than average within laboratory precisions, again following the pattern found for BAM RS3 and ECRM 752-1.

[41] The high contribution of Mg from silicate mineral phases in this material gave significant differences between centrifuged and noncentrifuged determinations (Figure 6a) and emphasized the importance of concurrent measurements of other element ratios to monitor silicate contamination (e.g., Al/Ca, Fe/Ca, Si/Ca, Ti/Ca), as recommended for checking cleaning efficiency when determining Mg/Ca in foraminiferal calcite [Barker *et al.*, 2003; Rosenthal *et al.*, 2004; Lea *et al.*, 2005]. The same number of laboratories determined Fe/Ca (Figure 6b) and Al/Ca ratios (Figure 6c) in CMSI 1767 as in ECRM 752-1, with a few participants providing results for Si/Ca and Ti/Ca and thirteen laboratories measuring Mn/Ca. Detailed results are included in the complete data set in auxiliary material Tables S1–S3. Fe/Ca ratios >1 mmol/mol were measured in CMSI 1767 in solutions without centrifuging (Figure 6b), falling to 0.67 mmol/mol on centrifuging, in agreement with the results of the preliminary homogeneity study. Al/Ca in this material was slightly higher than in ECRM 752-1 with a mean of 0.84 mmol/mol without centrifuging, falling to 0.23 mmol/mol

**Figure 4.** ECRM 752-1. Means of results from each laboratory, without statistical rejection: (a) Mg/Ca; (b) Fe/Ca; and (c) Al/Ca. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution. Error bars are  $\pm 2$  std errors on the mean from each laboratory. Red line in Figure 4a shows interlaboratory mean and standard deviation for centrifuged analyses before statistical rejection, including flow through analysis by Lab 29. Horizontal lines in Figures 4b and 4c show mean values of not centrifuged (blue) and centrifuged (red) data, not including Lab 29 (see text).





**Figure 5.** ECRM 752-1. Histograms of Mg/Ca results from each laboratory for solutions after centrifuging: (a) individual measurements from each laboratory and (b) comparison of results by ICP-MS and ICP-OES.

**Table 5.** Results From Each Laboratory for the Determination of Mg/Ca in CMSI 1767

Lab ID	Dissolution		Centrifuged Solutions					Not Centrifuged							
	Wt Solid (mg)	Volume (mL)	[Ca] ( $\mu\text{g/g}$ )	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n	[Ca] ( $\mu\text{g/g}$ )	Mg/Ca	SD	r.s.d. (%)	2 SE	n
1	50	40	500	100	5.459	0.030	0.55	0.025	6						
2	50	50	400							430	6.025	0.028	0.47	0.023	6
3	50	50	400	400	5.633	0.023	0.40	0.018	6	400	5.995	0.029	0.49	0.024	6
4	50–100	60	400–800	45	5.555	0.024	0.42	0.019	6	40	5.746	0.072	1.25	0.064	5
5	50	50	400	50	5.516	0.078	1.42	0.070	5	50	5.694	0.104	1.83	0.085	6
6	50	50	400	20	5.654	0.095	1.69	0.078	6	20	5.698	0.071	1.25	0.058	6
7	50	50	400							40	5.766	0.013	0.22	0.010	6
12	50	50	400	40	5.581	0.039	0.70	0.032	6	40	5.750	0.009	0.17	0.008	6
13	5	40	50	50	5.958	0.026	0.43	0.021	6	50	6.027	0.041	0.67	0.033	6
14	50	50	400	160	5.518	0.037	0.67	0.030	6	160	5.634	0.025	0.44	0.020	6
16	50	50	400	80	5.494	0.022	0.40	0.018	6	80	5.653	0.028	0.50	0.025	5
17	10	10	400	80	5.720	0.034	0.59	0.028	6	80	5.767	0.024	0.41	0.015	10
18	50	50	400	50	5.609	0.061	1.08	0.049	6	50	5.727	0.029	0.50	0.023	6
19	50	50	400	60	5.605	0.056	0.99	0.050	5	60	5.617	0.106	1.88	0.086	6
20	50	50	400	70	5.397	0.032	0.59	0.037	3	70	5.569	0.049	0.89	0.040	6
21	50	50	400	80	5.634	0.013	0.24	0.011	6	80	5.810	0.011	0.19	0.009	6
22	50	50	400	50	5.557	0.048	0.86	0.039	6	50	5.700	0.064	1.12	0.052	6
23	50	50	400	20	5.631	0.058	1.03	0.047	6	20	5.726	0.062	1.09	0.051	6
24	50	50	400	4	5.773	0.014	0.24	0.011	6	4	5.965	0.044	0.73	0.036	6
25	50	50	400	100	5.519	0.021	0.38	0.019	5	100	5.634	0.020	0.35	0.018	5
26	10	5	20 mM	160	5.757	0.040	0.69	0.032	6	160	5.688	0.051	0.89	0.041	6
29											5.557	0.075	1.35	0.087	3
30	50	50	400	100	5.725	0.047	0.81	0.038	6	100	5.687	0.048	0.84	0.042	5
31	40–74	50	300–600	50	5.392	0.017	0.32	0.014	6	50	5.528	0.021	0.39	0.017	6
33	50	50	400	1	5.401	0.065	1.21	0.053	6	1	5.625	0.103	1.83	0.084	6
All results (not including 29 with centrifuged)															
Mean (mmol/mol)					5.595	0.040	0.71	0.034		5.733	0.047	0.82	0.040		
s.d.					0.138					0.142					
r.s.d. (%)					2.46					2.47					
n					22					24					
>10 mg powder															
Mean					5.561	0.041	0.74	0.035		5.727	0.047	0.82	0.039		
s.d.					0.106					0.134					
r.s.d. (%)					1.91					2.34					
n					19					20					
After statistical data rejection including Lab 29															
Mean					5.556	0.038	0.67	0.033							
s.d.					0.104										
r.s.d.(%)					1.87										
n					19										

on centrifuging (Figure 6c). The flow through method (Lab 29) returned Al/Ca of 0.41 mmol/mol, lower than all except one of the not centrifuged determinations by other laboratories, but higher than all except one of the results after centrifuging (Figure 6c).

[42] Exclusion of results from the small ( $\leq 10$  mg) sample sizes used by laboratories 13, 17 and 26 from the reproducibility calculations in Table 5 reduced the mean Mg/Ca obtained and improved

the reproducibility, from Mg/Ca = 5.59 mmol/mol (0.14 s.d., 2.45% r.s.d) on 22 analyses to Mg/Ca = 5.56 mmol/mol (0.11 s.d., 1.91% r.s.d) on 19 analyses for centrifuged samples, implying that it is better to use sample weights >10 mg for this material. As found for both BAM RS3 and ECRM 752-1 centrifuging had little effect on Mn/Ca in CMSI 1767 with Mn/Ca = 0.069 mmol/mol (0.006 s.d., 9% r.s.d) found by 13 laboratories for determinations both with and without centrifuging.

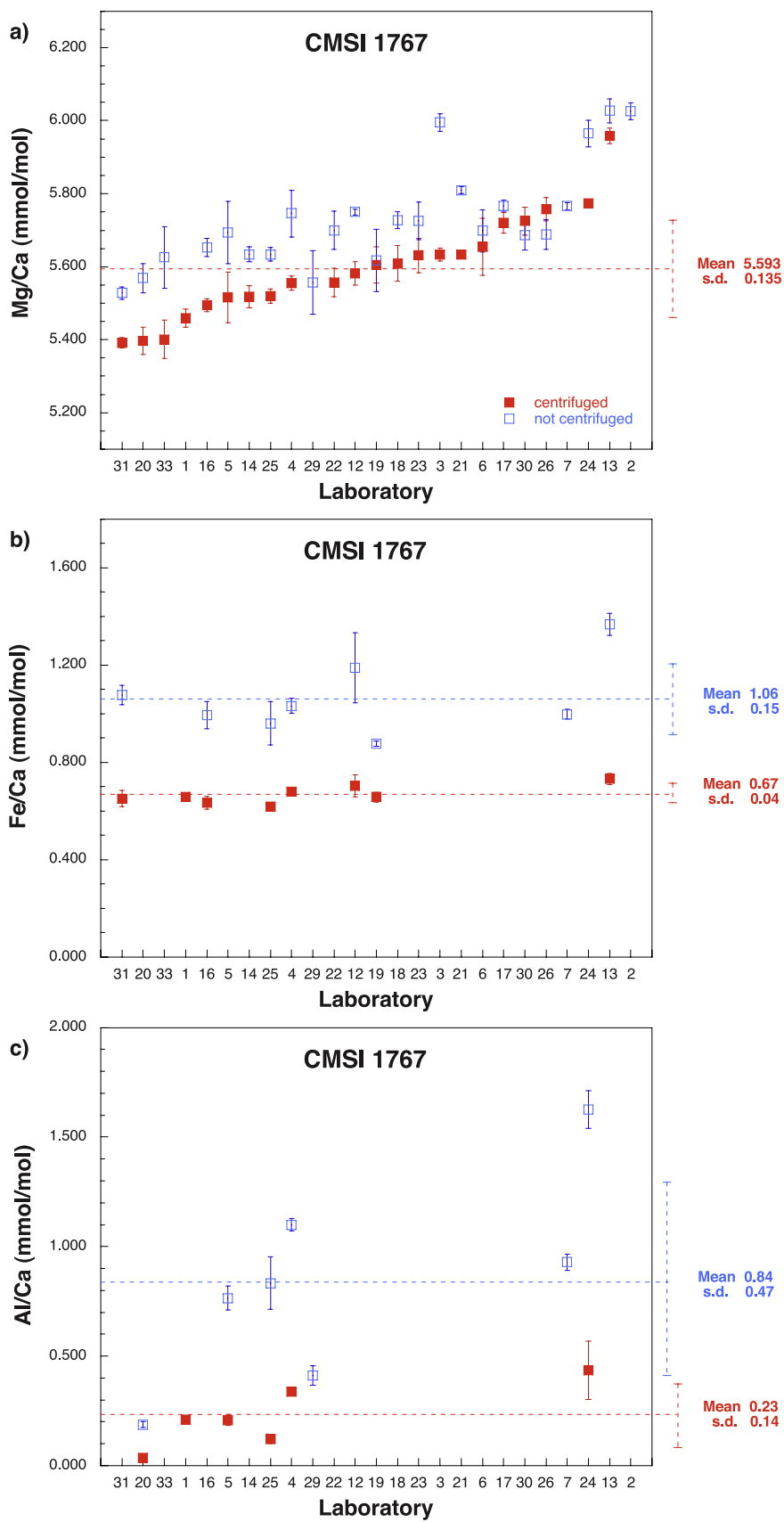


Figure 6

[43] Statistical analysis using the Cochran test rejects results from laboratory 6 from analyses after centrifuging, on the basis of the within laboratory variance (Table 5). After exclusion of results identified by the Cochran test, no outlying average values were found on application of the Grubbs test. The results following statistical data rejection using the Cochran test give Mg/Ca = 5.56 mmol/mol (0.11 s.d., 1.87% r.s.d) on 19 determinations, consisting of 18 determinations on >10 mg samples after centrifuging and including lab 29 (Table 5). Results of the analysis of variance (ANOVA) are presented and discussed with those from the other two materials in section 3.4. As found from analyses of the other materials, results obtained by ICPMS are statistically indistinguishable from those obtained by ICP-OES (Figure 7b).

[44] Twenty-one laboratories returned results of Sr/Ca determinations in CMSI 1767, twenty on solutions after centrifuging, twenty on solutions without centrifuging and one using the flow through method (Table 6). Mean values are plotted for each laboratory in Figure 8, in ascending order of centrifuged values, using data before statistical rejection. Within laboratory precisions averaged 0.54% on centrifuged solutions and 0.65% on solutions without centrifugation, excluding the flow through analyses of laboratory 29, or 0.80% including results of the flow through analysis (Table 6). Results with and without centrifuging solutions were in close agreement for all except two laboratories (18 and 30).

[45] The homogeneity of Sr/Ca within CMSI 1767 is demonstrated by results from the two laboratories where small samples ( $\leq 10$  mg) were dissolved, removal of these data having a negligible effect on the mean values shown in Table 6.

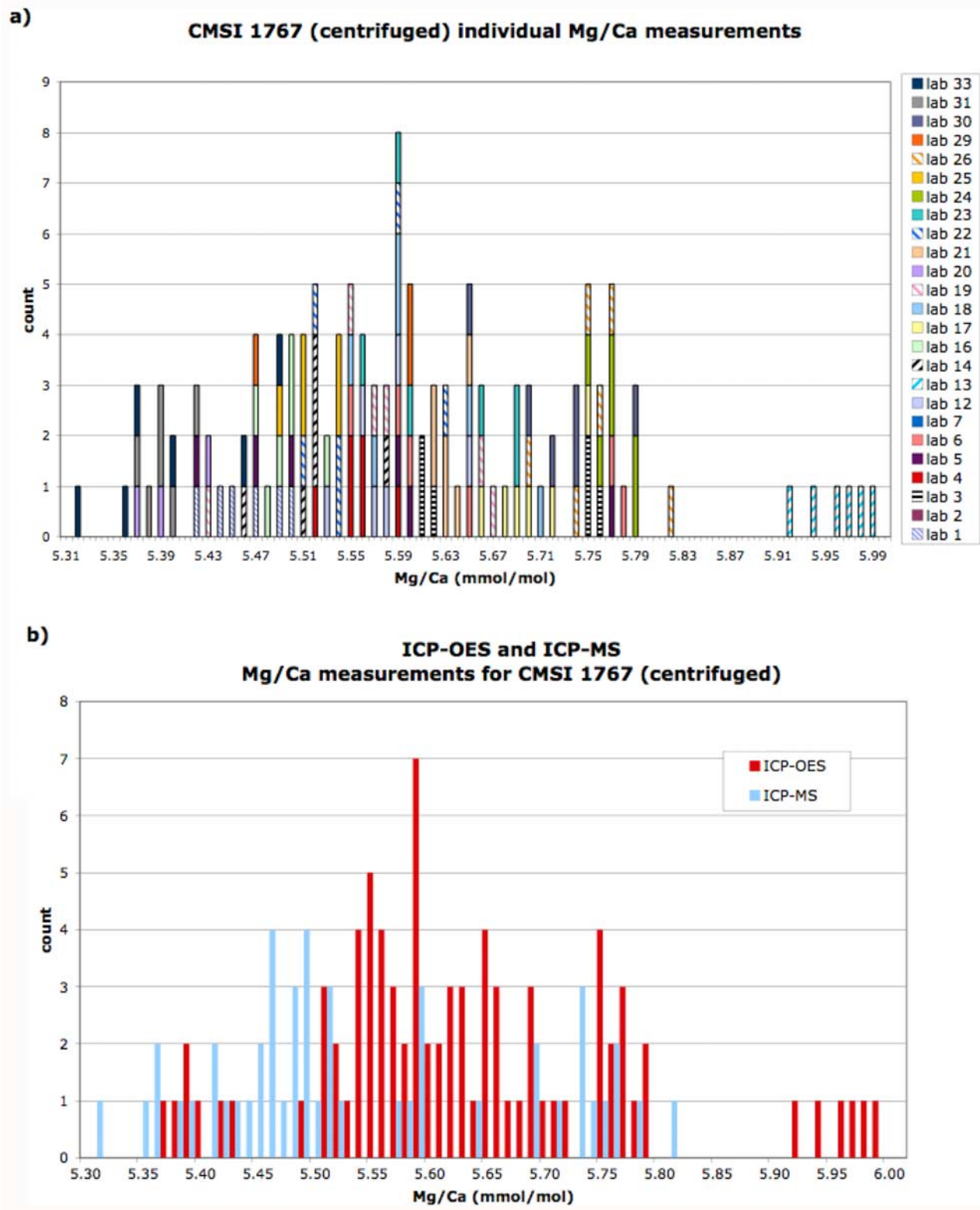
[46] Statistical analysis using the Cochran test rejected results on the basis of within laboratory variance from laboratory 29 for analyses without centrifuging, and from laboratories 6 and 23 for analyses after centrifuging (Table 6 and Figure 8). Application of the Grubbs test rejected the lowest set of values (Lab 22) giving Sr/Ca = 1.507 mmol/

mol (0.031 s.d., 2.06% r.s.d) on 17 determinations after centrifuging and Sr/Ca = 1.506 mmol/mol (0.036 s.d., 2.42% r.s.d) on 19 determinations without centrifuging (Table 6).

### 3.4. Comparisons Between the Three Materials

[47] The results of Mg/Ca determinations in the three materials are compared in Figure 9 using the Youden plot method [Kateman and Buydens, 1993]. The Mg contents of the materials are not close enough to treat them as Youden matched pairs [Horwitz, 1995; AOAC International, 2006] but comparison plots are informative. Mg/Ca measurements from solutions after centrifuging, including results from the flow through method (Lab 29), are plotted as two sample comparisons relative to ECRM 752-1 in Figures 9a and 9b for BAM RS3 and CMSI 1767, respectively. The large difference in Mg/Ca between BAM RS3 and ECRM 752-1 masks other effects; Figure 9a is dominated by “noise” and random scatter about the mean. Mg/Ca of CMSI 1767 and ECRM 752-1 are more similar, therefore the 1:1 line in Figure 9b plots closer to an angle of 45°, and Figure 9b emphasizes systematic differences between laboratories. The trend of the results in Figure 9b lies along the 1:1 line showing that in general laboratories obtaining a high, or a low, value relative to the mean in one material do so in the other, reflecting instrument calibrations among the laboratories. Outlying laboratories plot away from the trend followed by the other laboratories. For example, laboratory 19 returned a low value for Mg/Ca in ECRM 752-1 but was close to the mean for CMSI 1767 (and BAM RS3) whereas laboratory 26 returned a high value for CMSI 1767 and a value close to the mean for ECRM 752-1. This does not confirm whether values are correct, only that laboratories following the general trend are consistent. Figures 9c and 9d show the two sample comparison plots for BAM RS3 and CMSI 1767 after exclusion of Mg/Ca data from laboratory 19 for ECRM 752-1.

**Figure 6.** CMSI 1767. Means of results from each laboratory, without statistical rejection: (a) Mg/Ca; (b) Fe/Ca; and (c) Al/Ca. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution. Error bars are  $\pm 2$  std errors on the mean from each laboratory. Red line in Figure 6a shows interlaboratory mean and standard deviation for centrifuged analyses before statistical rejection, including flow through analysis by Lab 29. Horizontal lines in Figures 6b and 6c show mean values of not centrifuged (blue) and centrifuged (red) data, not including Lab 29 (see text).



**Figure 7.** CMSI 1767. Histograms of Mg/Ca results from each laboratory for solutions after centrifuging: (a) individual measurements from each laboratory and (b) comparison of results by ICP-MS and ICP-OES.

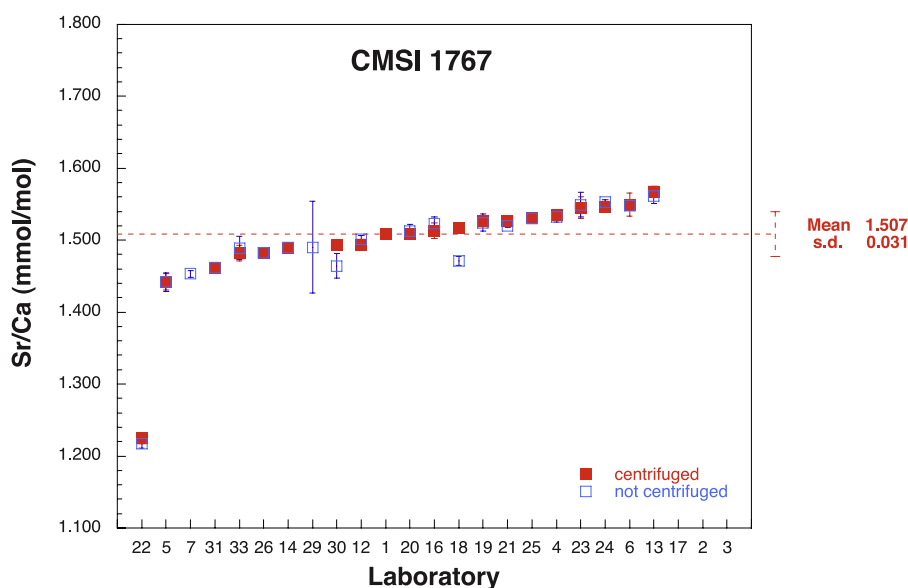
**Table 6.** Results From Each Laboratory for the Determination of Sr/Ca in CMSI 1767

Lab ID	Dissolution			Centrifuged Solutions						Not Centrifuged					
	Wt Solid (mg)	Volume (mL)	[Ca] ( $\mu\text{g/g}$ )	[Ca] ( $\mu\text{g/g}$ )	Sr/Ca	SD	r.s.d. (%)	2 SE	n	[Ca] ( $\mu\text{g/g}$ )	Sr/Ca	SD	r.s.d. (%)	2 SE	n
1	50	40	500	100	1.509	0.004	0.29	0.004	6						
2	50	50	400							430					
3	50	50	400	400						400					
4	50–100	60	400–800	45	1.535	0.005	0.34	0.004	6	40	1.532	0.008	0.55	0.007	6
5	50	50	400	50	1.442	0.013	0.91	0.011	6	50	1.442	0.015	1.06	0.013	6
6	50	50	400	20	1.549	0.019	1.25	0.016	6	20	1.548	0.007	0.48	0.006	6
7	50	50	400							40	1.453	0.007	0.46	0.005	6
12	50	50	400	40	1.494	0.007	0.44	0.005	6	40	1.501	0.006	0.41	0.005	6
13	5	40	50	50	1.567	0.010	0.63	0.008	6	50	1.561	0.013	0.82	0.010	6
14	50	50	400	160	1.489	0.003	0.19	0.002	6	160	1.490	0.003	0.23	0.003	6
16	50	50	400	80	1.513	0.014	0.92	0.011	6	80	1.523	0.011	0.75	0.009	6
17	10	10	400	80						80					
18	50	50	400	50	1.517	0.003	0.21	0.003	6	50	1.471	0.007	0.46	0.006	6
19	50	50	400	60	1.526	0.008	0.51	0.006	6	60	1.524	0.014	0.94	0.012	6
20	50	50	400	70	1.509	0.002	0.14	0.002	3	70	1.512	0.012	0.78	0.010	6
21	50	50	400	80	1.526	0.006	0.42	0.005	6	80	1.520	0.003	0.18	0.002	6
22	50	50	400	50	1.224	0.008	0.68	0.007	6	50	1.217	0.008	0.64	0.006	6
23	50	50	400	20	1.545	0.018	1.17	0.015	6	20	1.549	0.021	1.35	0.017	6
24	50	50	400	4	1.546	0.007	0.47	0.006	6	4	1.553	0.004	0.27	0.003	6
25	50	50	400	100	1.530	0.004	0.25	0.003	5	100	1.530	0.004	0.28	0.004	5
26	10	5	20 mM	160	1.483	0.006	0.38	0.005	6	160	1.483	0.007	0.47	0.006	6
29										1.490	0.056	3.74	0.064	3	
30	50	50	400	100	1.493	0.007	0.50	0.006	6	100	1.464	0.019	1.27	0.017	5
31	40–74	50	300–600	50	1.462	0.004	0.29	0.003	6	50	1.462	0.004	0.29	0.003	6
33	50	50	400	1	1.482	0.013	0.87	0.011	6	1	1.489	0.019	1.29	0.016	6
All results (not including 29 with centrifuged)															
Mean (mmol/mol)					1.497	0.008	0.54	0.007		1.491	0.012	0.80	0.011		
s.d.					0.071					0.072					
r.s.d. (%)					4.76					4.82					
n					20					21					
>10 mg powder															
Mean					1.494	0.008	0.55	0.007		1.488	0.010	0.65	0.008		
s.d.					0.073					0.076					
r.s.d. (%)					4.91					5.11					
n					18					18					
After statistical rejection															
Mean					1.507	0.007	0.46	0.006		1.506	0.010	0.65	0.008		
s.d.					0.031					0.036					
r.s.d. (%)					2.06					2.42					
n					17					19					

[48] Results of the analysis of variance (ANOVA) are presented in Table 7 for Mg/Ca in BAM RS3 determined with and without centrifuging solutions, Mg/Ca in ECRM 752-1 and Mg/Ca in CMSI 1767 from determinations on centrifuged solutions, including results of the flow through analysis technique, and Sr/Ca in CMSI 1767 for determinations both with and without centrifugation. The relevant unweighted statistics, intralaboratory and interlaboratory s.d. and r.s.d., have been included

in Table 7 for comparison with results of the ANOVA method.

[49] The intralaboratory repeatabilities ( $RSD_r\%$ ) for Mg/Ca determinations in centrifuged solutions range from 0.78% (CMSI 1767) to 1.15% (BAM RS3), becoming noticeably larger with decreasing Mg/Ca ratios. As found from the unweighted statistics, interlaboratory reproducibility ( $RSD_R\%$ ) when calculated from analysis of variance is considerably worse than intralaboratory repeatability



**Figure 8.** CMSI 1767. Sr/Ca means of results from each laboratory. Open symbols, not centrifuged; solid symbols, centrifuged after dissolution. Error bars are  $\pm 2$  std errors on the mean from each laboratory. Red line shows the mean value from 17 laboratories after statistical rejection.

( $RSD_r\%$ ), ranging from 4.45% (ECRM 752-1) to 8.73% (BAM RS3) for Mg/Ca determinations in solutions after centrifuging (Table 7). Similarly for Sr/Ca determinations in CMSI 1767, good intra-laboratory repeatability ( $RSD_r\%$ ) was obtained, 0.52% and 0.72% for centrifuged and not centrifuged solutions, respectively, but interlaboratory reproducibility ( $RSD_R\%$ ) was much worse at 5.05% and 5.92% for centrifuged and not centrifuged determinations, respectively.

[50] The interlaboratory reproducibilities include systematic errors from instrument calibrations within each laboratory and also any differences between the individual subsamples of material sent to the laboratories. However, the reproducibilities of determinations on material taken from five separate subsample bottles and analyzed by a single laboratory (Lab 25, Tables 3–6) show that inhomogeneity between subsamples is not significant. Interlaboratory variability is dominated by inconsistencies among instrument calibrations in the different laboratories.

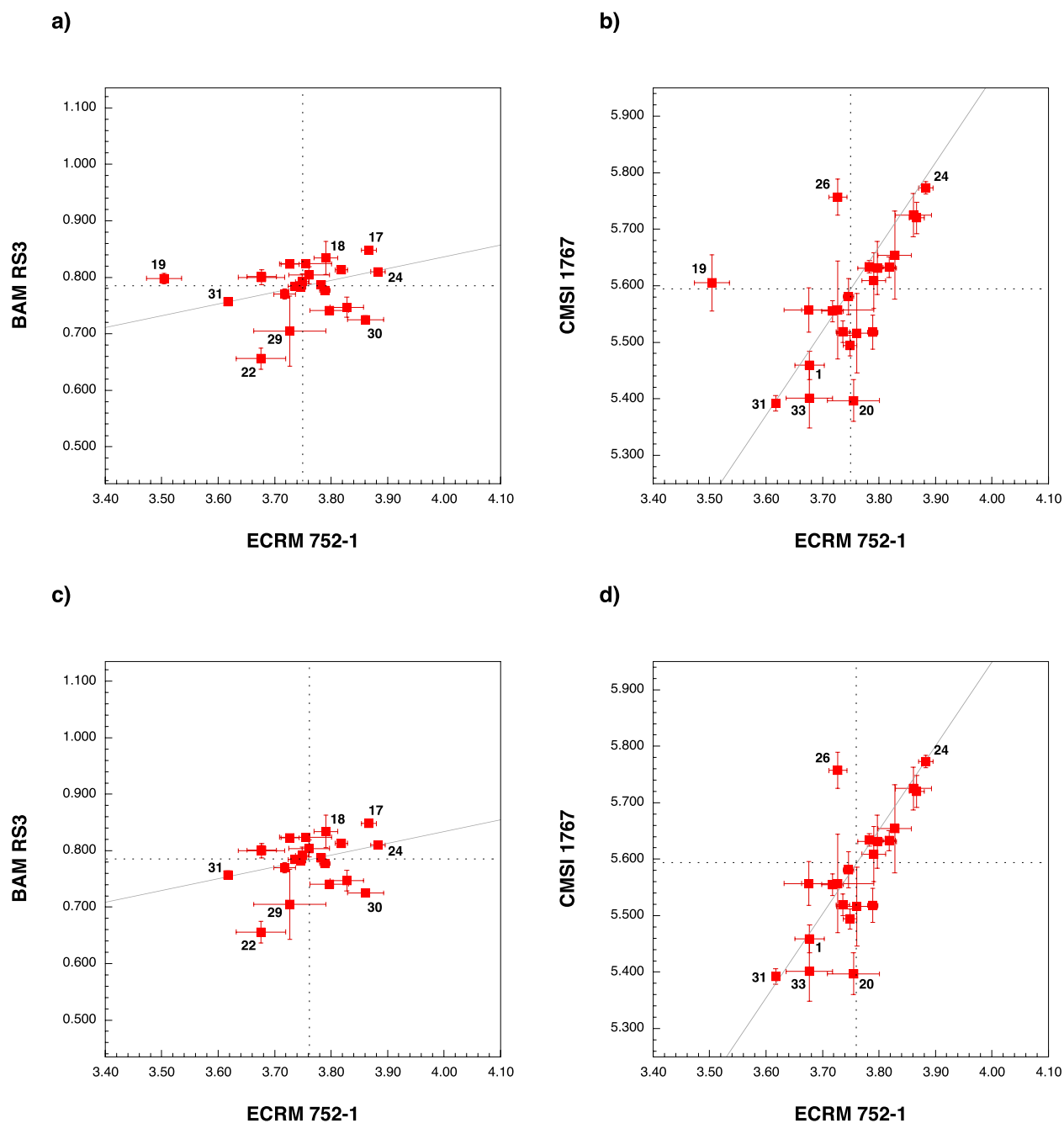
[51] Conversion of the interlaboratory reproducibilities ( $RSD_R\%$ ) to temperatures using the temperature calibration of *Anand et al.* [2003] gives overall reproducibilities of  $\sim 0.5^\circ\text{C}$  for Mg/Ca ratios of 3.76 and 5.56 mmol/mol (ECRM 752-1 and CMSI 1767) increasing to  $\sim 1.0^\circ\text{C}$  at Mg/Ca of 0.79 mmol/mol (BAM RS3), for a temperature

sensitivity of 9% per  $^\circ\text{C}$  [*Anand et al.*, 2003]. The repeatability ( $r$ ) and reproducibility ( $R$ ) represent the 95% confidence levels that two measurements are in agreement, within and between laboratories, respectively, assuming a normal distribution. Conversion of the reproducibility ( $R$ ) to temperature [*Anand et al.*, 2003] gives  $\pm 1.4^\circ\text{C}$  for Mg/Ca of 5.56 and 3.76 mmol/mol (CMSI 1767 and ECRM 752-1) increasing to  $\pm \sim 3^\circ\text{C}$  for Mg/Ca = 0.79 mmol/mol (BAM RS3 centrifuged) or  $\pm \sim 4^\circ\text{C}$  when calculated from reproducibility of BAM RS3 not centrifuged.

[52] Mg/Ca results for the three materials (Tables 3–5 and 7) are lower than calculated from certified element concentrations (Table 1) because in this study small sample sizes relevant to foraminiferal calcite were used for the determination of Mg/Ca in the carbonate fraction of the materials, whereas the certified element concentrations were determined on bulk material and represent the total contribution from all minerals present. This is reflected by the trace elements (Al, Fe, Si, Ti) which are low in carbonates and high in silicate mineral phases, and demonstrated by comparison of centrifuged and noncentrifuged determinations.

#### 4. Conclusions

[53] The results of Mg/Ca determinations in this study showed that repeatability ( $RSD_r\%$ ), for Mg/



**Figure 9.** Comparison plots of mean Mg/Ca results from each laboratory for determinations after centrifuging (including Lab 29): (a) BAM RS3 versus ECRM 752-1 and (b) CMSI 1767 versus ECRM 752-1. Error bars are  $\pm 2$  std errors on the mean from each laboratory. Dotted lines show the mean of all results for each sample. Gray solid lines are the 1:1 lines through the mean. (c and d) Same as Figures 9a and 9b, omitting Lab 19 Mg/Ca data for ECRM 752-1.

Ca determinations in solutions after centrifuging, increased with decreasing Mg/Ca, increasing from 0.78% at Mg/Ca = 5.56 mmol/mol (CMSI 1767) to 0.82% at Mg/Ca = 3.76 mmol/mol (ECRM 752-1)

and 1.15% at Mg/Ca = 0.79 mmol/mol (BAM RS3) as would be predicted for most analytical methods [Horwitz, 1982]. The average intralaboratory precisions concealed a wide range among



**Table 7.** Statistical Results of Analyses of the Materials Based on ANOVA Coefficients

Material Parameter Analyses	BAM RS3 Mg/Ca Centrifuged	BAM RS3 Mg/Ca Not Centrifuged	ECRM 752-1 Mg/Ca Centrifuged	CMSI 1767 Mg/Ca Centrifuged	CMSI 1767 Sr/Ca Centrifuged	CMSI 1767 Sr/Ca Not Centrifuged
Laboratories retained	18	22	21	19	17	19
Not retained	3	3	1	4	4	2
Mean	0.791	0.777	3.762	5.560	1.507	1.506
Median	0.795	0.779	3.767	5.558	1.509	1.509
Intralaboratory SD	0.008	0.008	0.027	0.038	0.007	0.010
Intralaboratory RSD%	0.95%	1.03%	0.72%	0.67%	0.46%	0.65%
Interlaboratory SD	0.030	0.043	0.069	0.104	0.031	0.036
Interlaboratory RSD%	3.79%	5.52%	1.83%	1.86%	2.06%	2.42%
S <sub>r</sub> (repeatability SD)	0.009	0.016	0.031	0.043	0.008	0.011
RSD <sub>r</sub> %	1.15%	2.06%	0.82%	0.78%	0.52%	0.74%
Repeatability r	0.026	0.045	0.086	0.121	0.022	0.031
S <sub>R</sub> (reproducibility SD)	0.069	0.102	0.168	0.248	0.076	0.089
RSD <sub>R</sub> %	8.73%	13.09%	4.45%	4.47%	5.05%	5.92%
Reproducibility R	0.193	0.285	0.469	0.696	0.213	0.250
Reason for exclusion of laboratories						
Sample size	-	-	-	13,17,26	-	-
Cochran test	6, 18, 22	19, 29, 33	0	6	6, 23	29
Grubbs test	0	0	0	0	22	22
Youden plot	-	-	19	-	-	-

laboratories (Tables 3–5). Interlaboratory reproducibilities (RSD<sub>R</sub>%) were noticeably worse than intralaboratory repeatabilities, again increasing at low Mg/Ca, from 4.5% at Mg/Ca = 5.56 mmol/mol and 3.76 mmol/mol (CMSI 1767 and ECRM 752-1) to 8.7% at Mg/Ca = 0.79 mmol/mol (BAM RS3), for Mg/Ca determinations in centrifuged solutions. The interlaboratory variability is dominated by inconsistencies among instrument calibrations between laboratories, which need to be addressed to improve compatibility of Mg/Ca measurements and calculated temperatures. This is particularly important when determining temperatures from the low Mg/Ca ratios associated with benthic and cold-water planktonic species of foraminifera.

[54] This study confirmed the suitability of the circulated solid standards as reference materials for foraminiferal Mg/Ca determinations, provided that appropriate procedures are adopted in order to minimize and to monitor possible contamination from silicate mineral phases present in ECRM 752-1 and CMSI 1767. The combination of Mg/Ca determinations in ECRM 752-1 and CMSI 1767

(Figures 9b and 9d) represents an efficient way of achieving analytical consistency among laboratories, with the objective of minimizing deviations from the mean values obtained by the community. BAM RS3 was shown to be a valuable reference material for determinations at low Mg/Ca ratios, being homogenous with a pure CaCO<sub>3</sub> matrix. We recommend that laboratories determining low Mg/Ca ratios report results for BAM RS3 to improve compatibility of low temperature estimates. CMSI 1767, because of its high silicate mineral content, is the most difficult of the three materials for Mg/Ca determinations but has the advantage of an ideal Sr/Ca ratio for intercalibration of foraminiferal Sr/Ca.

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