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Evaluation of a ^{42}Ca–^{43}Ca double-spike for high precision Ca isotope analysis

K. Gopalan [a,b,*], D. Macdougall [a], C. Macisaac [a]

[a] Geosciences Research Division, Scripps Institution of Oceanography, La Jolla, CA 92093-0220, USA
[b] National Geophysical Research Institute, Uppal Road, Hyderabad 500007, India

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Abstract

Use of a ^{42}Ca–^{43}Ca double-spike for Ca isotopic analysis on Thermal Ionization Mass Spectrometers (TIMS) offers two important advantages over the ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca double-spikes that are currently used to correct for instrumental mass fractionation according to the exponential law. First, since the normalizing (^{42}Ca/^{43}Ca) and the corrected (^{44}Ca/^{40}Ca) ratios differ in their average mass by only 0.5 mass unit, they will tend to fractionate coherently thereby minimizing errors in the corrected ratio due to any deviation of the actual machine fractionation from an exponential law. Secondly, all four isotopes (40–44) required for the analysis can be measured simultaneously in modern multi-collector TIMS. This will eliminate errors in mass fractionation correction caused by rapid fluctuations or drifts in fractionation and will also reduce analysis time substantially. We report here initial data for laboratory standards and seawater using a ^{42}Ca–^{43}Ca double-spike that show how these advantages lead to more consistent and faster Ca isotopic analysis than hitherto possible.

Keywords: Ca isotopes; TIMS; Double-spike

1. Introduction

Studies of mass dependent fractionation of Ca isotopes as a tracer of geologic, oceanographic and biologic processes have been limited by the poor analytical precision relative to the very restricted range of fractionation so far observed in natural materials [1]. The observed maximum range of natural fractionation is ∼1‰ per mass unit, or ∼4‰ in the conventionally measured ratio, ^{44}Ca/^{40}Ca. The mass dependent fractionation during mass spectrometric measurements is much larger—about five times as large for Thermal Ionization Mass Spectrometer (TIMS) analyses and much more for Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS). This instrumental bias is best corrected in TIMS measurements using the double-spike technique [2]. For MC-ICPMS, repeated sample–standard comparisons are used [3]. TIMS has the advantage of freedom from isobaric interferences, but requires both more time for each analysis (several hours in single-collector mode) and tedious and time-consuming sample preparation prior to mass spectrometry. MC-ICPMS is much faster and requires minimal sample preparation effort, but suffers from very large mass fractionation and serious isobaric interferences. Analytical uncertainty is typically quoted as ±0.1–0.2‰ at the 2σ level in the ^{44}Ca/^{40}Ca ratio using either approach, although there are very few data in the literature that give details of the repeat measurements on which these claims are based.

The latest review of Ca isotopic variations in natural materials [1] shows that there are only about six laboratories worldwide involved in such studies, and the number of publications in the last decade is small. DePaolo [1] concludes that wider applications of Ca isotope measurements in geochemistry would be possible if measurement reproducibility could be improved to ±0.05–0.03‰. He suggests that this could be achieved with a new generation of multi-collector TIMS or MC-ICPMS.

The most challenging technical problem in using MC-ICPMS for Ca isotopic analysis is the elimination of and/or precise correction for elemental and molecular isobaric interferences from many sources on almost every Ca isotope, and ensuring very stable mass bias and background. Modern approaches [4,5] use quantitative separation of Ca from the sample matrix, extreme care in matching sample and standard solutions, desolvating nebulizers to reduce the formation of oxides and hydroxides, ‘cold

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* Corresponding author.
E-mail address: gopalank1@rediffmail.com (K. Gopalan).

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plasma' to minimise Ar-based interferences, dynamic reaction cells for drastic reduction of ^{40}Ar ions and finally high resolution mass spectrometry to separate the residual molecular interferences from the Ca isotopes of interest. Despite these strategies the best precision so far achieved for Ca analysis on modern MC-ICPMS is just about equal to that using TIMS with double-spike correction for mass fractionation. Because its technology is rapidly evolving, MC-ICPMS may soon facilitate more precise and accurate measurements, although the instruments demand a high level of technical competence for reliable operation. TIMS, on the other hand, is a more mature technology and achievement of higher precision for Ca isotope analysis most likely requires development of thermal ionization sources with low mass fractionation even for light elements, better understanding of the physics and chemistry of the fractionation process, and optimization of double-spikes in terms of both their isotopic constitution and composition (e.g., [6,7]).

In this report, we present initial measurements to test the potential advantages of a ^{42}Ca–^{43}Ca double-spike for higher precision and faster Ca isotopic analysis on TIMS—the instrument of choice or necessity in many laboratories.

2. Present status of Ca isotope measurements

Russell et al. [2] were the first to achieve a precision of ±0.5‰ in the ^{44}Ca/^{40}Ca ratio using a ^{42}Ca–^{48}Ca double-spike to correct for instrumental fractionation. Their significant contribution to experimental methodology was not so much the use of a double-spike to correct for machine fractionation (this technique was already well known) but the recognition that an exponential rather than the conventional linear or power law best describes fractionation of Ca isotopes in TIMS. If an exponential law is an exact description of the isotopic fractionation process, it can be used to accurately correct mass fractionation between any pair (i, j) of isotopes using the observed fractionation between any other pair (u, v) of isotopes of the same element, independent of the magnitude of fractionation [8]. However, Jungck et al. [9] observed small but significant departures from a strict exponential law when they used the ^{44}Ca/^{40}Ca ratio to correct ^{48}Ca/^{40}Ca in unspiked Ca samples using TIMS. They reported a significant and systematic drift (a few parts per ten thousand) in the corrected ^{48}Ca/^{40}Ca ratios with varying fractionation during an analytical run, and hence resorted to a modified exponential law (by truncating terms higher than second order in the expansion series) to bring the residual dependence of correction within experimental error. Hart and Zindler [10] also found that Ca isotope fractionation in TIMS does not exactly match an exponential law and proposed that mixing between independently fractionating reservoirs in the sample layer was responsible for the small deviations they observed.

If the actual fractionation during measurement deviates from an exponential law, then corrected ratios will be in error. In this context, it is instructive to consider Wasserburg et al.'s [8] calculation of the error that would result by correcting measured Nd isotope ratios using the power law if the exponential law were the true fractionation law. When normalized to ^{150}Nd/^{142}Nd (mean mass 146), ^{142}Nd/^{144}Nd ratios (mean mass 143) show a significant correlation with mass fractionation, but ^{148}Nd/^{144}Nd ratios (mean mass 146, the same as the normalizing pair) do not show any such correlation. This suggests that a practical and effective approach to closely track small and variable deviations of the actual fractionation from the strict exponential law is to match the mean masses of the normalizing and normalized ratios as closely as possible. More recent results by Vance and Thirwall [11] corroborate this conclusion. These workers report that mass bias in their MC-ICPMS analyses of Nd isotopes deviates substantially from an exponential fractionation law, and they conclude that unless the average mass of the normalizing and normalized isotope pairs match, the accuracy and precision of corrected ratios are seriously degraded. They attribute this to the more coherent fractionation of two isotope ratios with about the same mean mass. Note that although these data refer to Nd, the large fractionation that occurs even for heavy isotopes in MC-ICPMS analyses is comparable to that for Ca using TIMS (up to 1.5% per mass unit).

The mismatch between the mean masses of the normalizing and normalized Ca isotope ratios is just 2 mass units in the internal normalization procedure followed by Jungck et al. [9] and Hart and Zindler [10]. Apparently even this small difference can result in residual dependence of exponentially corrected ratios on fractionation. On the other hand, Nelson and McCulloch [12], also using a normalizing pair for which the mean mass differed by 2 mass units from the corrected pair, did not find any detectable drift of corrected ratios in their measurements of natural Ca. However, they report a very large discrepancy between internal and external precision, the latter being five to six times worse than the former. As they used large sample loads (up to 25 μg Ca) and short (multi-collector) analysis times, this difference could possibly be due to mass bias being relatively stable during each run but variable from run to run.

Most of the laboratories that measure Ca isotopes using TIMS have used either ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca double-spikes for mass bias corrections. The former tracer, with a ^{42}Ca/^{48}Ca ratio of 5.2083, was first used by Russell et al. [2]. It has since been used by Skulan et al. [13], Zhu and Macdougall [14] and Lemarchand et al. [15], but with quite different ^{42}Ca/^{48}Ca ratios. The ^{43}Ca–^{48}Ca double-spike has been used by three European laboratories in Germany, Switzerland and France, respectively [16,17]. Using this approach, both ^{40}Ca/^{44}Ca and ^{42}Ca/^{44}Ca ratios can be measured in natural samples. The mean masses of these tracer pairs differ by 3 and 3.5 mass units, respectively, from that of the ^{40}Ca/^{44}Ca pair, which is the corrected ratio that is usually reported. If a mismatch in mean mass of just 2 mass units can cause resolvable errors in exponential mass fractionation correction as reported by Jungk et al. [9] and Hart and Zindler [10], then a difference of 3 or 3.5 mass units should result in even larger errors. Surprisingly, this has not been quantitatively assessed in published reports so far. An obvious manifestation of such an error would be a pronounced residual dependence of normalized ratios on mass bias during a run. Russell et al. [2] included possible contributions from changing fractionation and inadequacy of the exponential law in the external precision of 0.05% in their analyses. Zhu and Macdougall [private communication] noted a systematic variation in corrected ^{44}Ca/^{40}Ca ratios in many of their sample runs, and resorted to the modified exponential law of Jungck et al. [9] to bring such drifts within analytical error.

In order to examine this effect, we used different normalizing pairs to correct the ^{44}Ca/^{40}Ca ratio for mass bias under the identical fractionation conditions of a single mass spectrometer run. The ^{42}Ca–^{43}Ca tracer solution we prepared for this work also contains ^{48}Ca in comparable abundance (see next section). We measured masses 40, 42, 43, 44 and 48 in single-collector mode for several mixtures of the tracer with the SIO Ca standard and corrected each measured ^{44}Ca/^{40}Ca for mass bias using the grand means of the measured ^{42}Ca/^{48}Ca, ^{43}Ca/^{48}Ca and ^{43}Ca/^{40}Ca ratios (note that the latter has the same average mass difference from ^{44}Ca/^{40}Ca as does ^{42}Ca/^{43}Ca, but is subject to smaller statistical error). The mean masses of these four ratios differ by 3, 3.5 and 0.5 mass units, respectively, from that of the ^{44}Ca/^{40}Ca ratio. We show a linear fit to the exponentially corrected ^{44}Ca/^{40}Ca ratios for two such runs in Fig. 1. The in-run fractionation change was much more during the analysis of Mix 15 (measured ^{44}Ca/^{40}Ca ratios increasing by about 3% from beginning to end) than in the case of Mix 16 (about 1% increase in ^{44}Ca/^{40}Ca). Fig. 1 clearly demonstrates that drift in the corrected ratios increases with both mismatch in average mass and fractionation.

In summary, there is considerable evidence that straightforward application of the exponential law for mass bias correction in TIMS Ca isotope analysis may degrade accuracy and precision when the average masses of the normalizing and normalized isotope pairs differ significantly. Until a law more representative of the true fractionation process in TIMS is found, a practical and effective way to get around this problem is to match the average masses of the relevant ratios as closely as possible. It is worth noting in this context that double-spikes used for many other stable isotope measurements by TIMS (e.g., Cr, Fe, Zn, Se

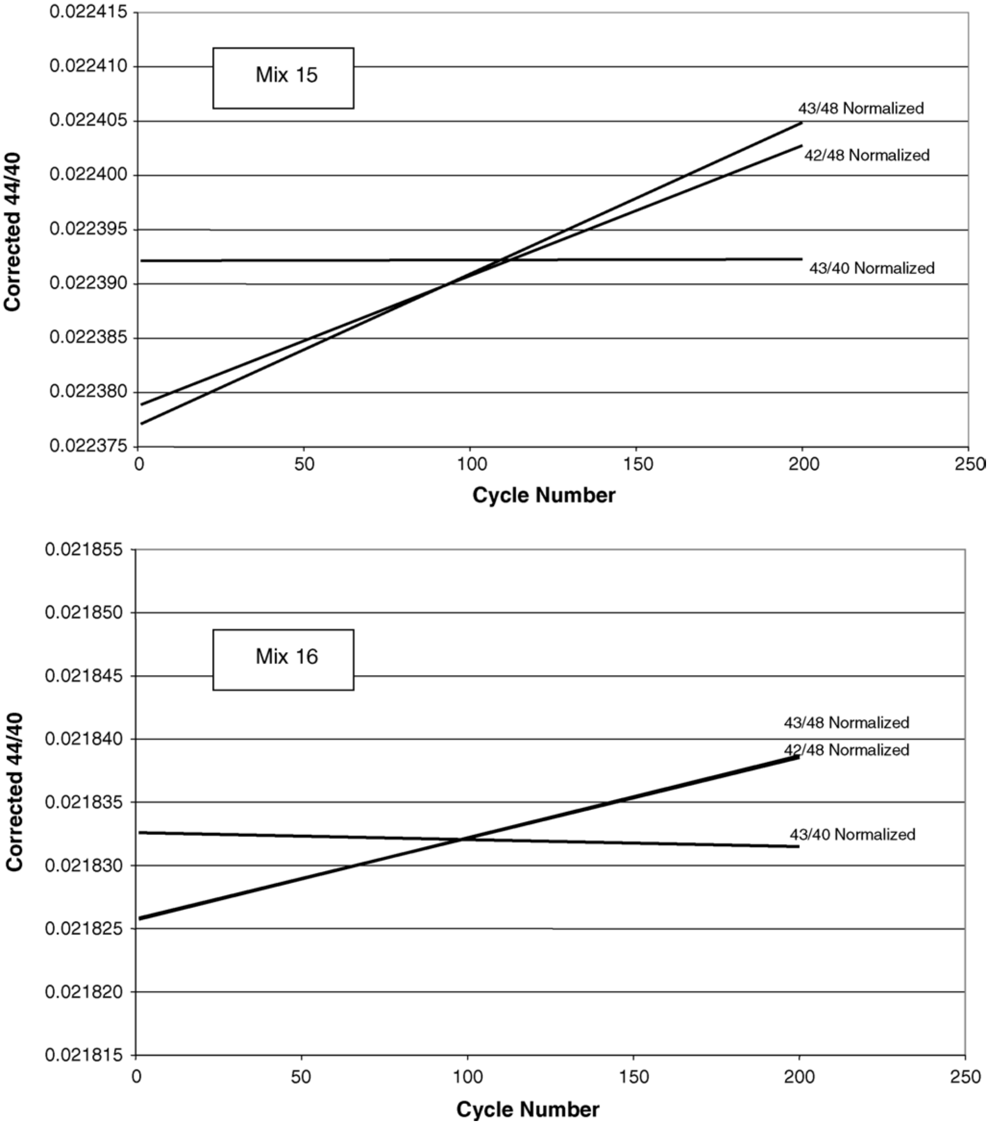

Fig. 1. Variation of measured ^{44}Ca/^{40}Ca ratios normalized to three different ratios using the exponential law with varying fractionation during two different mass spectrometric runs. The change in fractionation during one run (upper panel) was about three times greater than in the other (lower panel). Residual dependence of corrected ratios on mass fractionation is the least with ^{43}Ca/^{40}Ca correction in either case.

and Mo) match the targeted ratios very closely in mean mass. For Ca, both ^{42}Ca–^{48}Ca and ^{43}Ca–^{48}Ca tracers fall considerably short of this requirement. Considering the available enriched Ca isotopes, two favourable choices are: a ^{42}Ca–^{46}Ca double-spike to correct ^{48}Ca/^{40}Ca ratio, and a ^{42}Ca–^{43}Ca double-spike to correct the conventionally targeted ^{44}Ca/^{40}Ca ratio. In this work, we evaluate the analytical feasibility of the latter, which, in addition to differing by just 0.5 mass unit in the relevant average masses, provides a compelling advantage over other double-spikes for multi-collector measurements.

3. Analytical procedures

For this feasibility study, we prepared small quantities of ^{42}Ca–^{43}Ca spike by mixing an aliquot of the stock solution of the La Jolla ^{42}Ca–^{48}Ca spike [14] with a solution containing calcium enriched in ^{43}Ca (approximately 83% enriched, obtained from Oak Ridge National Laboratory). Two different mixtures with approximately equal abundances of ^{42}Ca and ^{43}Ca were prepared for use in the laboratories of the co-authors at the Scripps Institution of Oceanography, La Jolla, CA (SIO), and the National Geophysical Research Institute, Hyderabad, India (NGRI). The double-spike used at SIO was calibrated against the SIO Ca laboratory standard, whereas that used at NGRI was calibrated against the NIST SRM 915a Ca standard. For the NGRI calibration, the reference Ca isotopic composition of Russell et al. [2] was assumed for SRM 915a. The isotopic compositions of the standards (assumed), ^{43}Ca spike (certified) and the two double-spikes (measured) are given in Table 1. The uncertainty in the ^{42}Ca/^{43}Ca ratio in the double-spikes, relative to respective standards, is less than 0.2%.

In order to test the efficacy of the ^{42}Ca–^{43}Ca double-spike, a series of doubly spiked standards as well as doubly spiked seawater aliquots were analyzed both at NGRI and SIO. The sample–spike proportions were adjusted so that in most cases about 90% of the ^{43}Ca in the mixture was contributed by the spike. This resulted in approximately equal abundances of ^{42}Ca, ^{43}Ca and ^{44}Ca in the mixture, and ensured that measurement uncertainties in the ratios of these isotopes to ^{40}Ca were similar. However, this may not be the optimal mixture in other respects.

For mass spectrometric analysis at SIO, between 600 and 1000 ng of Ca was sandwiched between layers of Ta_2O_5 melange [18] on a tungsten filament. At NGRI either 500 or 1000 ng of Ca was first mixed with Ta_2O_5 melange and then loaded onto a rhenium filament. At SIO, all measurements were made using a VG Sector 54 TIMS, while at NGRI measurements were made on a VG 354. For single-collector measurements, the ^{40}Ca ion current was maintained between 5.4 and 6.6×10^{-11} A. At SIO the measurement sequence was 46.5 (baseline)–40–42–43–44–46.5, with integration times of 5 s for 46.5, 42, 43 and 44 and 1 s for 40, with a magnet settling time of 2 s. ^{39}K was monitored to be less than 10^{-13} A prior to the start of an analysis session. In most cases, 300 sets of ratios were measured, with beam centering after each block of 10 scans and focusing every 5 blocks. At NGRI the measurement sequence was 44.5 (baseline)–40–41–42–43–44–44.5, with integration times of 4 s for 42, 43 and 44, 1 s for 40 and 41 and 10 s for baseline. Measurement at mass 41 both allowed monitoring of ^{41}K and provided additional time (3 s) for the ^{40}Ca beam to decay to a negligible level. Beam centering and focusing were done after each block of 10 scans and a run included at least 200 sets of ratios. At SIO, a series of multi-collector analyses was also carried out. For these the ^{40}Ca current was maintained between 8 and 12×10^{-11} A, measured on collector L4 using a 10^{10} Ω resistor. A single sequence was used to measure ^{40}Ca, ^{42}Ca, ^{43}Ca and ^{44}Ca simultaneously with an integration time of 5 s. Collector gains were monitored frequently; no significant changes were observed during the time over which measurements were made.

Table 1
Isotopic compositions of standards and double-spikes

	^{42}Ca/^{40}Ca	^{43}Ca/^{40}Ca	^{44}Ca/^{40}Ca
SRM 915a	0.006621[a]	0.001376[a]	0.0212076[a]
SIO Ca standard[b]	0.006701	0.0014	0.0217
^{43}Ca spike[c]	0.04414	6.7078	0.2689
SIO ^{42}Ca–^{48}Ca[d]	11.6164	0.00817	0.06356
SIO ^{42}Ca–^{43}Ca	4.86898	3.70849	0.17256
NGRI ^{42}Ca–^{43}Ca	2.91725	3.86414	0.169851

[a] Russell et al. [2] reference ratios.
[b] Jungck et al. [9].
[c] ORNL certified values.
[d] Zhu and Macdougall [14].

Data analysis followed conventional procedures for double-spike measurements. The three measured ratios, ^{42}Ca/^{40}Ca, ^{43}Ca/^{40}Ca and ^{44}Ca/^{40}Ca, with very similar ion statistical uncertainties, were used offline to solve for the three unknowns: the sample/spike ratio (“Q”), the instrumental bias factor (“p”) and the sample ^{44}Ca/^{40}Ca ratio. The three simultaneous equations containing transcendental terms for exponential correction of mass bias are difficult to solve algebraically [19] and hence are usually solved iteratively [2,13,16]. Our iterative routine is very similar to that of Heuser et al. [16] based on an algorithm originally given by Compston and Oversby [20] for lead isotopic analysis. This routine, which we have implemented both as an Excel spreadsheet and as a simple Matlab data reduction program, provides a feel for the rapidity of convergence to the final solution.

The average measured isotope ratios from a run can be used directly in an iterative double-spike correction, as was done by Lemarchand et al. [15]. We preferred to first correct the measured ratios for in-run machine fractionation before double-spike calculations. We used the grand mean of the measured ^{43}Ca/^{40}Ca ratio for normalization, rather than ^{42}Ca/^{43}Ca, as the latter gives a larger statistical error in the normalized ratios, which is propagated in subsequent calculations. The mean masses of both pairs differ from the mean mass of the corrected pair – ^{44}Ca/^{40}Ca – by the same amount, 0.5 mass unit. This initial in-run normalization facilitates screening of the corrected ratios for any residual dependence on fractionation, and allows for rejection of distinct outliers and assessment of analytical precision free of fractionation effects. The mean values of the fractionation-corrected measured ratios obtained in this way are used in subsequent calculations. Firstly, a first approximation to the sample/spike ratio, Q, is calculated from the measured ^{44}Ca/^{43}Ca ratio, and the known ^{44}Ca/^{43}Ca ratios in the spike and standard, using the Ca standard composition to represent the unknown sample composition. Secondly, the value of Q obtained in this way is used to calculate a first approximation to the unfractionated (true) ^{42}Ca/^{43}Ca ratio in the mixture using the spike, standard, and mean of the in-run corrected ^{42}Ca/^{43}Ca ratios. Comparison of this first approximation to the measured ratio provides a first approximation to the fractionation parameter p (p corresponds to the exponent 'beta' in the equation for the exponential law in [8]), which is then used to correct the other measured ratios for machine fractionation. Thirdly, subtraction of the small spike contribution from the fractionation-corrected ^{44}Ca/^{40}Ca ratio in the mixture gives a first approximation to the true ^{44}Ca/^{40}Ca ratio of the unspiked sample. Finally, this first approximation sample ^{44}Ca/^{40}Ca ratio is compared with its assumed (laboratory standard) value to facilitate correction of the sample ^{42}Ca/^{40}Ca and ^{43}Ca/^{40}Ca ratios. The second cycle of iteration starts with the once-corrected measured and sample ^{44}Ca/^{43}Ca ratios to calculate a second approximation for Q, and the other steps follow as described above. As already mentioned, this procedure closely follows that developed by Compston and Oversby [20] for lead isotopic analysis. In our work, iterations are continued until all the corrected ratios stabilize to within 0.01‰, invariably within five cycles.

4. Results

Analytical data from our two laboratories for multiple analyses of the NIST carbonate standard SRM 915a, the La Jolla laboratory standard and Ca separated from seawater are given in Tables 2a–2c. In addition to the calculated ^{44}Ca/^{40}Ca ratio, we also list the grand mean of the measured ^{43}Ca/^{40}Ca ratios in each run. This provides an estimate of the sample/spike ratio in each mixture and also the variation of fractionation both between replicate runs on the same filament load and among different filament loads. Note that there is no observable dependence of the

Table 2a
NGRI single-collector data

Standard[a]	^{43}Ca/^{40}Ca[b] (measured)	^{44}Ca/^{40}Ca[c] (sample)	Seawater[a]	^{43}Ca/^{40}Ca[b] (measured)	^{44}Ca/^{40}Ca[c] (sample)
1a	0.035960	0.0212077	1a	0.038094	0.0212483
1b	0.036460	0.0212070	1b	0.038732	0.0212500
2a	0.039214	0.0212108	2a	0.037422	0.0212451
2b	0.040044	0.0212066	2b	0.037724	0.0212523
3a	0.019392	0.0212103	3a	0.040082	0.0212478
3b	0.019701	0.0212098	3b	0.040684	0.0212455
4a	0.024208	0.0212086	4a	0.026223	0.0212526
4b	0.024618	0.0212117	4b	0.026280	0.0212476
5a	0.020534	0.0212102	5a	0.028850	0.0212467
5b	0.020712	0.0212080	5b	0.030208	0.0212467
6	0.028985	0.0212085	6a	0.029396	0.0212509
			6b	0.029864	0.0212460
			7a	0.031070	0.0212475
			7b	0.031602	0.0212513

[a] Separate loads of NIST 915a carbonate standard or seawater, except that those labeled a, b, etc., are consecutive runs of the same load.
[b] Mean of the raw measured values for the run, typically 200 ratios.
[c] Calculated iteratively as explained in the text, assuming Russell et al. [2] values for NIST 915a Ca standard.

Table 2b
SIO single-collector data

Standard[a]	^{43}Ca/^{40}Ca (measured)[b]	^{44}Ca/^{40}Ca (sample)[c]	Seawater[a]	^{43}Ca/^{40}Ca (measured)[b]	^{44}Ca/^{40}Ca (sample)[c]
LJ1	0.021447	0.0217020	1	0.023816	0.0217343
LJ2	0.019716	0.0217014	2	0.024135	0.0217322
LJ3	0.023461	0.0217019	3	0.017891	0.0217332
LJ4	0.023178	0.0217056	4	0.023975	0.0217325
LJ5	0.023324	0.0217008	5	0.023699	0.0217311
LJ6	0.023374	0.0217082	6	0.023314	0.0217337
LJ7	0.023473	0.0217066	7	0.023144	0.0217305
LJ8	0.023292	0.0217056	8	0.023550	0.0217316
LJ9	0.023385	0.0217076	9	0.023307	0.0217339
LJ10	0.023806	0.0217039	10	0.023324	0.0217287
LJ11	0.024059	0.0217045	11	0.023200	0.0217312
LJ12	0.023981	0.0217034	12	0.023391	0.0217300
			13	0.023347	0.0217323

[a] Separate loads of the SIO laboratory standard or seawater.
[b] Mean of the raw measured values for the run, typically 250 ratios.
[c] Calculated iteratively as explained in text, relative to the assumed Ca isotopic composition in the Ca laboratory standard.

Table 2c
SIO static multi-collector data

Standard[a]	^{43}Ca/^{40}Ca (measured)[b]	^{44}Ca/^{40}Ca (sample)[c]	Seawater	^{43}Ca/^{40}Ca (measured)[b]	^{44}Ca/^{40}Ca (sample)[c]
LJ1	0.022811	0.0216911	1	0.022997	0.0217223
LJ2	0.022837	0.0216910	2	0.023391	0.0217244
LJ3	0.022857	0.0216928	3	0.023015	0.0217212
LJ4	0.023031	0.0216916	4	0.023164	0.0217245
LJ5	0.022960	0.0216917	5	0.023230	0.0217196
LJ6	0.022891	0.0216915	6	0.023322	0.0217242
LJ7	0.022824	0.0216897	7	0.023313	0.0217227
LJ8	0.022873	0.0216939	8	0.023423	0.0217240
LJ9	0.022967	0.0216913	9	0.023237	0.0217235
LJ10	0.022932	0.0216943	10	0.029177	0.0217255
LJ11	0.022963	0.0216940	11	0.029049	0.0217234
LJ12	0.028849	0.0216916			
NIST 1	0.024026	0.0216804			
NIST 2	0.024029	0.0216803			
NIST 3	0.023935	0.0216821			
NIST 4	0.023916	0.0216836			

[a] Separate loads of the SIO laboratory standard (“LJ”) or NIST SRM 915a (“NIST”).
[b] Mean of the raw measured values for the run, typically 200 ratios.
[c] Calculated iteratively as explained in the text, relative to the assumed Ca isotopic composition of the Ca laboratory standard.

calculated ^{44}Ca/^{40}Ca values on the spike/sample ratio within the range of spike amounts used.

As our main aim in this work was only to test the viability of the ^{42}Ca–^{43}Ca double-spike, we have not carried out a detailed assessment of error propagation through the data reduction procedure. In any case, as has been pointed out by other workers, the true measure of uncertainty in the calculated ^{44}Ca/^{40}Ca values is the reproducibility of replicate analyses (external error), which we discuss below.

The data in Tables 2a–2c show considerable differences in the calculated ^{44}Ca/^{40}Ca values for the same materials (e.g., seawater or SRM 915a) between measurements made at SIO and NGRI. This is because the Russell et al. [2] value of 0.021208 for ^{44}Ca/^{40}Ca was assumed for SRM 915a in the NGRI laboratory, and 0.0217 for the La Jolla laboratory standard in the SIO laboratory. The values (not absolute) assumed for the standards do not significantly affect the relative difference between two materials, for example, between the NIST SRM 915a standard and seawater. These agree well between the two laboratories and between our results and those of others reported in the literature. In addition, the data in Tables 2b and 2c show differences between the calculated values for single- and multi-collector data from the SIO laboratory. In this case, the difference is likely due to collector efficiencies and absolute gain values. We did not attempt to adjust efficiencies to ensure matching of the results. Again, the important parameter is the relative difference between different materials, which is the same within analytical uncertainties for both single- and multi-collector results.

5. Discussion

Fig. 1 shows quite clearly that Ca isotope analysis by TIMS is subject to in-run fractionation that is not completely accounted for by the exponential law. It also shows that this residual effect is dependent on the magnitude of the fractionation, and on the isotope pair chosen for normalization. It appears to be minimized by the choice of a normalizing isotope pair with a mean mass close to that of the corrected pair. Thus, using a ^{42}Ca–^{43}Ca double-spike should increase the accuracy and precision of ^{44}Ca/^{40}Ca measurements.

The data in Tables 2a–2c indicate that measurement reproducibility using the ^{42}Ca–^{43}Ca double-spike is equal to or better than that reported in the literature using ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca spikes. For example, for the SIO single-collector results (Table 2b), the standard deviations for the laboratory standard (12 runs) and seawater (13 runs) analyses are just over 0.1‰ (1σ). The total range is slightly more than twice this, at 0.34‰ for the standards and 0.26‰ for seawater. For the NGRI data (Table 2b), both standard deviations and total range are larger if all runs of each sample are included, but if multiple runs are averaged the data are comparable to those from SIO. Our multi-collector analyses exhibit a restricted total range that appears to be slightly better than for the single-collector data (Table 2c). Twelve standard measurements exhibit a total range of 0.21‰, while 11 seawater analyses have a total range of 0.28‰. The external uncertainty, or reproducibility, is thus in the range of ±0.15‰ or better for a single measurement.

Most other laboratories report uncertainties of 0.1–0.2‰ but measure each sample multiple times to obtain such reproducibility, and anecdotal evidence coupled with our own experience using the ^{42}Ca–^{48}Ca spike suggests the regular occurrence of unexplained “outliers” considerably beyond this range. An external precision better than 0.015% after double-spike correction seems to be a very optimistic estimate, as such precision even with internal normalization is not better than 0.015%. The data in Tables 2a–2c represent all analyses conducted for this work, with no removal of outliers. For direct comparison with the results reported here, there is only one published detailed quantitative report on reproducibility, that by Heuser et al. [16].

These authors report a large number of measurements of both a CaF_2 standard and the NIST 915a carbonate standard using a ^{43}Ca–^{48}Ca spike and a multi-collector procedure (data in their Fig. 8). While the 1σ standard deviation in both cases is approximately 0.22‰, the total range of all measured values – the best measure of reproducibility or external error – is very large, between 1.2 and 1.4‰. This means that the uncertainty for a single sample measurement is a large fraction of the natural isotopic variability. Heuser et al. [12] also report (in a separate figure, their Fig. 7) 10 single-collector analyses and about 80 multi-collector analyses for NIST SRM 915a for which the total range is much smaller than for their other data, about 0.4‰. It is not clear from the text what the relationship is between the two sets of analyses.

As a test of the accuracy of our results, we compare the relative values measured for different materials using the ^{42}Ca–^{43}Ca spike with the same differences measured using other spikes. Hippler et al. [21] measured seawater Ca isotopic composition relative to NIST SRM 915a and reported a value (in the conventional delta notation) of $\delta^{44}Ca = 1.88 \pm 0.04\ \mathrm{mil}^{-1}$ (2σ standard error). For the NGRI data in Table 2a, comparison of the seawater and SRM 915a mean values (0.0212485 and 0.0212090, respectively) yields $\delta^{44}Ca = 1.86 \pm 0.12$ (1σ), in excellent agreement with the Hippler et al. [21] value. At SIO, the NIST standard was not measured by single collector, but static multi-collector data include four runs for SRM 915a. Relative to the mean value of these runs, the seawater mean value gives $\delta^{44}Ca = 1.88 \pm 0.09$, the standard deviation corresponding to the standard deviation of the 11 seawater values. Thus, the seawater − SRM 915a difference is consistent between our two laboratories and the data of Hippler et al. [21].

Although use of the ^{42}Ca–^{43}Ca tracer minimizes non exponential mass bias effects, it requires that fractionation measured over just one mass unit be used to correct the ratio of an isotope pair separated by 4 mass units. Thus, to attain a given precision in the targeted ratio, the precision of measurement of $^{42}Ca/^{43}Ca$ must be higher than that required using ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca tracers. A quantitative assessment of error propagation as a function of the data reduction algorithm, spike composition, spike/sample proportion and uncertainties in measured isotope ratios could lead to substantially better results than we have reported here. We note that no such analysis is available for any of the Ca double-spike combinations currently in use.

Simultaneous measurement of Ca masses using multi-collector TIMS is an obvious way to increase measurement precision. However, mass dispersion in modern multi-collector machines is typically adequate for analysis over only four masses in the Ca range. This means that all required isotopes (40–44) can be measured simultaneously when the ^{42}Ca–^{43}Ca double-spike is used, but that at least two cycles are required for either the ^{42}Ca–^{48}Ca or ^{43}Ca–^{48}Ca double-spikes. Simultaneous measurement of all required isotopes in the case of the ^{42}Ca–^{43}Ca double-spike eliminates any uncertainties caused by variability in the rate of change of mass bias—not uncommon in Ca analysis. In the case of both the ^{42}Ca–^{48}Ca and ^{43}Ca–^{48}Ca double-spikes, the two isotopes of the normalizing pair must be measured in separate sequences separated by (typically) 5 s or more. Measurement of all isotopes in a single multi-collector sequence also results in the shortest possible analysis time, and hence also minimizes the total range of fractionation during a run.

Fletcher et al. [22] and Heuser et al. [16] have carried out multi-collector Ca analyses but do not find a significant improvement in reproducibility relative to single collection. Skulan et al. [13] report that multi-collector runs result in excellent internal precision but poor external precision possibly due to subtle differences in focus conditions in the ion source from sample to sample. The results reported here show clearly that external precision for multi-collector analysis using the ^{42}Ca–^{43}Ca double-spike equals or exceeds that for single-collector analysis.

6. Conclusions

We show that use of a ^{42}Ca–^{43}Ca double-spike for TIMS calcium isotope analysis provides two critical advantages over the conventionally used pairs, ^{42}Ca–^{48}Ca and ^{43}Ca–^{48}Ca. First, the average mass of the ^{42}Ca–^{43}Ca pair is 42.5, only 0.5 mass unit different from the isotope pair to be fractionation corrected, $^{44}Ca/^{40}Ca$. This leads to more accurate mass bias corrections using the exponential law. Secondly, in contrast to the other double-spike pairs, all required masses can be measured in a single multi-collector sequence using the ^{42}Ca–^{43}Ca double-spike, thus eliminating errors that arise from rapid fluctuations or drifts of instrumental mass bias. In addition, use of a single measurement sequence greatly reduces total analysis time and hence the range of in-run fractionation.

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