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Optimization of double spike technique using peak jump collection by Monte Carlo method: an example for the determination of Ca isotope ratios

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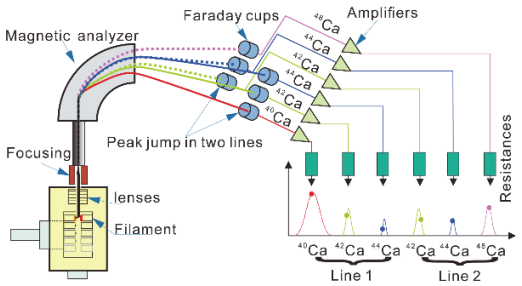
Content entry

Monte Carlo method is used to estimate the additional uncertainty of measured value introduced by peak jump mode for Ca isotope ratios determination.



Abstract

Three important factors, including the choice of an appropriate spike isotope pair, the composition of double spike, and the ratio of double spike to sample, have been proven to have significant effect on the precision of the double spike technique. Moreover, peak jump (i.e., dynamic) collection mode is frequently used, which could lead to more variable parameters such as cup configurations, ratio combinations and integration times in different jump lines. In order to optimize the above conditions under the peak jump mode, a Monte Carlo method that simulates uncertainties from Johnson noise and counting statistics is applied for the prediction of the precisions of measured results using double spike technique. As an example, this model was used to predict the possibility for cup configurations and ratio combinations of three double spike pairs of ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca, respectively, in two jump lines. Predicted internal precisions improved 25%, 20% and 25% by using ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca double spike, respectively, under optimized conditions. The theoretical predicted optimum precision was verified by repeatedly measuring two standards of NIST SRM 915a and NIST SRM 915b using ^{42}Ca-^{48}Ca double spike over several months. The observed internal precisions of δ^{44}Ca in these two standards are in good agreement with the predicted internal precisions, validating the effectiveness of the proposed Monte Carlo technique. The observed external precisions in two standards are 8-9 times poorer than the internal precisions, properly due to an extra uncertainty source. Nevertheless, the optimal ratio combination yields the best external

precision. As demonstrated, the proposed Monte Carlo simulation is an effective method to predict the optimal cup configurations, ratio combinations and integration times for double spike technique using peak jump collection mode.

Keywords: Double spike technique, Monte Carlo simulation technique, Peak jump collection mode

Introduction

Double spike technique is widely used for the determination of non-traditional stable isotopic compositions of natural samples. Natural variation in non-traditional stable isotopic composition is usually small, for example only about 4‰ for $\delta^{44}Ca$[1, 2] and 6.4% for $\delta^{98}Mo$[3]. Thus, characterization of non-traditional stable isotope demands the most accurate and precise double spike technique to investigate these small isotopic differences in natural samples. The double spike technique was established by the early works of Dodson.[4, 5] It is a solution that could solve the instrumental and natural fractionation of samples simultaneously with use of three isotope ratios constructed from the abundance of four isotopes in double spike, sample and mixture, respectively.[6] Great efforts have been made in the last decade to improve the accuracy and precision of this technique. It has been verified that the choice of an appropriate double spike isotope pair, the composition of double spike, and the proportion of double spike in the mixture are the key factors to dominate the precision of the double spike technique.[7-9] Meanwhile, the optimum double spike predicted by theoretical models have been successfully used in various practical applications. The term optimum double spike collectively refers to the optimum choice of the double spike isotope pair, the composition of double spike, and the proportion of double spike in the mixture. For example, Rudge *et al.*[7] firstly reported theoretical optimum double spikes for 33 elements, which were confirmed by a good agreement between the predicted and observed value of $\delta^{56}Fe$ ratio measurements. Subsequently, John *et al.*[8] further

improved the precision up to 30% for double spike-MC-ICPMS (DS-MC-ICPMS) technique by using an independent variation of sample and double spike concentration, and successfully predicted the optimal proportion of double spike in mixture for the determination of δ^{56}Fe, δ^{66}Zn and δ^{114}Cr. Moreover, Lehn *et al.*[9] optimized the ^{42}Ca-^{43}Ca double spike by not only considering the optimal double spike, but also taking the Faraday cup deterioration effect into account when utilizing double spike TIMS (DS-TIMS) analysis for Ca isotope ratios, and achieved an excellent external precision of ~0.04‰ (2σ) for δ^{44}Ca. Clearly, prediction of the precision of measurements is useful to understand the complex uncertainty propagation process of double spike technique.

In previous studies,[7-8] all isotopes were considered being collected simultaneously in their predicted models and confirmed by practical applications which were implemented under static collection mode. However, peak jump collection mode (i.e., dynamic) is often used for the implementation of double spike technique,[10-14] which leads to more variable parameters such as cup configurations, ratio combinations and independent integration times in different magnetic jump lines. Lehn *et al*.[9] first introduced peak jump collection model into their prediction model for precision, but these parameters were not fully explored due to concerns about possible damage of collectors.

In this study, a Monte Carlo technique that simulates uncertainties from Johnson noise and counting statistic following the optimization model presented in the previous studies[7-9] was used to estimate measurement precisions of variable cup configurations, ratio

combinations and integration times under peak jump collection mode. Three Ca double spike pairs: ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca were investigated using the above Monte Carlo simulation technique, to discover how these instrument setting parameters impact on the analysis precision, and find out the optimum settings for these parameters. These double spike pairs were chosen because of the large mass dispersion between isotopes ^{40}Ca and ^{48}Ca, which cannot be collected simultaneously. The feasibility of this estimation model was verified by the determination of standards spiked with ^{42}Ca-^{48}Ca double spikes. The observed internal and external precisions of the δ^{44}Ca ratio of two standards of NIST SRM 915a and NIST SRM 915b were compared with the predicted precisions, respectively.

Precision prediction model

Uncertainty sources

There are two different quantifiable uncertainties during data collection by TIMS, which can induce the uncertainty of measured value of individual isotope: one is Johnson noise associated with the detector, also known as 'hot noise'; and the other is counting statistics of the ion beam, also known as 'shot noise'. The variation of individual isotope is normally distributed within a standard deviation of the stochastic uncertainty with a mean value of its real intensity. According to the previous reports, [7-9] Johnson noise is only related to the integration time when the resistance (R) associated with the amplifier is specified. The absolute uncertainty due to Johnson noise can be expressed in Eq. 1:[7-9]

$$\sigma^{i}_{Johnson\ noise} = \sqrt{\frac{4kTR}{\Delta t_i}} \quad (1)$$

where k is Boltzmann constant of 1.3806504×10^{-23} J K^{-1}, i is the label of the 4 isotopes involved in the inversion (i = 1, 2, 3 or 4), T is the temperature of the amplifier at 300 K, R is the resistance associated with amplifier, defaulted by 10^{11} Ω (consistent with instrumental setting) and Δt_i is the integration time. The absolute uncertainty due to counting statistics is expressed in Eq. 2:[7-9]

$$\sigma^{i}_{counting\ statistics} = \sqrt{\frac{eRV_i}{\Delta t_i}} \quad (2)$$

where e is the elementary charge of $1.602176487\times10^{-19}$ C and V_i is the ion beam intensity. Finally, the uncertainty associated with each measured individual isotope is:

$$\sigma^{i}_{uncert} = \sqrt{\left(\sigma^{i}_{Johnson\ noise}\right)^2 + \left(\sigma^{i}_{counting\ statistics}\right)^2} \quad (3)$$

Uncertainty propagation

The uncertainty model indicates that the uncertainty of signal intensity of each isotope is associated with the ion beam intensity (V_i) and the integration time (Δt_i). The mean total ion beam intensity (V) is defined as the sum intensity of the involved four isotopes. Individual isotope intensity (V_i) is related to its abundance in the mixture, which in turn to the composition of spike and the proportion of spike in the mixture. The composition of double spike (T) is calculated by the proportion of two single spikes (PSA, PSB) as the following equation:

$$T_i = q \times PSA_i + (1-q) \times PSB_i \quad (4)$$

where q is the proportion of PSA_i in double spike, PSA_i and PSB_i are the abundance of isotope i in PSA and PSB, respectively. Similarly, the composition of mixture (M) can be calculated by the proportion of double spike and sample (N):

$$\mathrm{M}_i = p \times T_i + (1-p) \times N_i \quad (5)$$

where p is the proportion of the double spike in the mixture and N_i is the abundance of isotope i in the sample. Here the "Russell value" [15] (Table. 1) was adopted as the initiate sample composition (N_i) for the double spike iteration. The intensity of each of the four isotopes (V_i) can be calculated by its relative abundance and the sum abundance of these four isotopes in the mixture as the following equation:

$$\mathrm{V}_i = VM_i \frac{1}{\sum_i M_i} \quad (6)$$

The uncertainty of signal intensity of each isotope is calculated by using σ^i_{error} multiplying by a random number of R_{nom}, which is normally distributed with a mean value of 0 and a standard deviation of 1. Thus, the measured signal intensity of each isotope can be simulated by adding this uncertainty to its real value:

$$\mathrm{V}^{\mathrm{i}}_{\mathrm{M}} = V_i + \sigma^i_{uncert} R_{nom} \quad (7)$$

Under static collection model, every isotope is only measured once and can be simply simulated by the above equations. However, it is more complicated when peak jump mode is used. Although the measured values of the same isotope in different lines are from the

same ion beam (have equal V_i), they are independent of each other for the stochastic uncertainties. Consequently, these independent measured values (IMVs) that were measured in different lines have independent uncertainties. According to Eqs. (1), (2), (3), and (7), IMVs can be simulated by using independent Δt_i and R_{nom}, respectively, while using the same V_i, since they were from same ion beam but measured in different lines.

Monte Carlo uncertainty estimation

For double spike calculation, three ratios constructed from the measured values of four isotopes can be solved by either algebraic[7] or iterative[9, 10] approach to obtain the natural composition of the sample. As described above, under static collection mode each isotope was only measured once, with no extra measurement uncertainty. As a result, only one combination of three isotope ratios is needed for the double spike calculation ratios constructed from only four measured values, and any isotope can be used as the denominator. When peak jump collection mode is used, additional uncertainty is brought by IMVs compared to those measured under static collection mode. It is clear that the cup configuration determines which isotope can have IMVs, while the ratio combination determines the uncertainty of which IMVs will pass through the uncertainty propagation procedure. Thus different cup configurations and ratio combinations can be simulated by using different IMVs to construct three ratios. In this study three double spike pairs: ^{42}Ca-

^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca were investigated to demonstrate the simulation procedure of different cup configurations and ratio combinations by using IMVs.

Because of the complexity in solving the double spike calculation and in the estimation of the precision of δ^{44}Ca ratio, Monte Carlo technique was applied to simulate the uncertainty propagation. In this study, Monte Carlo technique was carried out in an Excel spreadsheet. Once three Ca ratios required for double spike calculation are identified, different double spike data reduction approaches generate the same δ^{44}Ca value. Here we adopted the equation presented in Lehn *et al.*[9] to calculate double spike iteration. For the purpose of obtaining accurate simulate results, 5000 simulated analyses were used in each simulation. At this level, the variation of predict results of δ^{44}Ca was less than 0.005‰ (one standard deviation). The internal precision was determined by doubling the standard error of the mean result ($2\sigma_{SEM}$), with the assumption of 100 data scans as actual measurements.

Experimental

Instrumentation

All Ca isotope measurements were performed on a Triton TIMS (Thermo Finnigan, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources in China University of Geosciences, Wuhan. This instrument is equipped with nine Faraday cups connected with nine rotatable virtual amplifies which help eliminate

gain calibration biases. The resistor of each amplify is 10^{11} Ω as default. Rhenium filaments assemblies were outgassed at 1 A for one hour, and then at 4 A for another hour at a 10^{-6} mbar condition.

Reagents and samples

Nitric acid was purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a DST-1000 acid purification system (Savillex, Eden Prairie, USA). 20% H_3PO_4 used to load sample was prepared by dilution of Suprapur® grade ortho-Phosphoric acid (Merck KGaA, Darmstadt, Germany) with deionized water. All the dilutions and cleaning procedures were carried out with deionized Milli-Q water (Millipore, Billerica MA, USA). Two Ca carbonate powder isotopic reference materials, NIST SRM 915a and NIST SRM 915b, were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg MD, USA). The total Ca blank was typically less than 10ng, negligible compared to the amount of Ca processed.

Analysis of Ca isotopes

Filament loading protocol from Holmden *et al.*[16] and Lehn *et al.*[9] was followed. Instead of using single filament, double filaments arrangement was adopted to achieve lower mass fractionation and more stable ion beams.[17] In brief, a current of 1.4 A was passed through the filament, and Parafilm™ was gently swiped on either side of the filament, helping constrain the sample droplet. Then 1 μL of spiked sample solution containing 3 μg Ca was carefully loaded onto the centre of the filament in three droplets. After all the droplets were

dried at 1 A, 1 μL of 20% H_3PO_4 was loaded on the filament, and the mixture droplet was dried at 1.6 A. Finally, the electrical current was increased until a weak red glow was visible, followed by shutting down of the electrical current.

Ca isotopes intensities were acquired in peak jump mode for all spiked samples using the cup configuration listed in Table 2. The sample heating was performed using an automated heating program, allowing fully automated measurements. Intensity of ^{40}Ca was maintained at about 9 V to achieve 10 V of total (^{40}Ca, ^{42}Ca, ^{44}Ca and ^{48}Ca) signal intensity. Detailed instrument settings for the measurements are listed in Table 2.

Results and discussion

Effect of cup configuration and ratio combination

There is a large mass dispersion in Ca isotopes, i.e., 20% relative mass dispersion for ^{40}Ca to ^{48}Ca, which exceeds the limitation of most modern multi-collector mass spectrometry. Therefore, six Ca isotopes ranging from the lowest mass ^{40}Ca to the highest mass ^{48}Ca cannot be collected simultaneously. An alternative is to separate Ca isotopes into two lines by collecting ^{40}Ca to ^{46}Ca in the low mass line first and collecting ^{42}Ca to ^{48}Ca in the high mass line using peak jump method (Fig. 1). For example, peak jump collection using two lines was employed with use of ^{42}Ca-^{48}Ca double spike[11, 18] or ^{43}Ca-^{48}Ca double spike[10, 19]. Although the use of double spike pair of ^{46}Ca-^{48}Ca has not been reported, measurements are still possible by using two lines peak jump collection mode. Consequently, IMVs of

^{42}Ca, ^{43}Ca, ^{44}Ca and ^{46}Ca generate many possibilities of cup configurations and ratio combinations. Under two peak jump lines, there are up to two different isotopes having IMVs for each double spike pair. Note that when ratios are constructed from different lines, additional uncertainties may arise from signal fluctuations (through quadratic drift correction), contributing extra uncertainties to the measured precision of δ^{44}Ca. In this study, only ratios constructed from the same line are considered for the estimation. Therefore, no more than five measured values of four isotopes can be used to construct three ratios, and IMVs of two isotopes (e.g. ^{42}Ca and ^{44}Ca) cannot be employed to construct ratios at the same time.

Our original objective was to identify the most effective conditions for Ca isotope ratios determination among these various cup configurations and ratio combinations. To achieve this, we listed all the potential cup configurations, including five collectors in two lines (Fig. 1 a, b, c and d). Correspondingly, there were four different ratio combinations utilizing different IMVs: (A_1-A_3) $^{40}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{44}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{48}Ca_{\#2}/^{4i}Ca_{\#2}$ (i = 2, 3 or 6); (B_1-B_3) $^{40}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{44}Ca_{\#2}/^{4i}Ca_{\#2}$, $^{48}Ca_{\#2}/^{4i}Ca_{\#2}$; ($C_1$-$C_3$) $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#1}/^{44}Ca_{\#1}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$; ($D_1$-$D_3$) $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#2}/^{44}Ca_{\#2}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$. For the purpose of the acquisition of optimal cup configuration and ratio combination, Monte Carlo technique was used. Measurement internal precisions were predicted for 8s of integration time for each line and 10V for the total signal intensity using A-D ratio combinations. Static collection mode was investigated using ratio combinations: (E_1-E_3) $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#1}/^{44}Ca_{\#1}$,

$^{48}Ca_{\#1}/^{44}Ca_{\#1}$, in order to compare to those of peak jump collection mode. The predicted internal precisions ($2\sigma_{SEM}$) of $\delta^{44}Ca$ values using ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca double spike pairs are shown in Fig. 2 respectively.

Our results showed that with use of any double spike pair of ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca, the predicted internal precisions of $\delta^{44}Ca$ of peak jump collection varied from those of static collection. The best predicted internal precisions of $\delta^{44}Ca$, using ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca double spikes and peak jump collection for Ca ratios using configurations of C_1, A_2 and D_3, were improved by 20%, 25% and 10%, respectively, compared to those estimated by using static mode E_1, E_2 and E_3. These results indicated that the additional uncertainties generated by using peak jump collection mode had an impact on the predicted internal precision of $\delta^{44}Ca$. However, optimal double spike areas did not change significantly between peak jump and static collection mode in nearly all cases. Thus, the optimal double spike estimated under static collection mode condition is suitable for measurements operated under peak jump collection mode.

On the other hand, the optimal cup configuration and ratio combination is different for individual double spike pair. With the use of ^{42}Ca-^{48}Ca double spike, the best predicted internal precision of $\delta^{44}Ca$ can be obtained by using C_1 ratio combination (i.e., $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{42}Ca_{\#1}/^{44}Ca_{\#1}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$). This ratio combination indicates that the best cup configuration with use of ^{42}Ca-^{48}Ca double spike should be ranged for measurements of ^{40}Ca, ^{42}Ca, and ^{44}Ca in the first line and only ^{44}Ca and ^{48}Ca in the second line. Similarly,

for ^{43}Ca-^{48}Ca double spike, the best predicted internal precision can be obtained by using the ratio combination A_2 (i.e., $^{40}Ca_{\#1}/^{43}Ca_{\#1}$, $^{44}Ca_{\#1}/^{43}Ca_{\#1}$, $^{48}Ca_{\#2}/^{43}Ca_{\#2}$) and measuring ^{40}Ca, ^{43}Ca and ^{44}Ca, and ^{43}Ca and ^{48}Ca in the first and second lines, respectively. For ^{46}Ca-^{48}Ca double spike, the best predicted internal precision can be obtained by using the ratio combination D_3 (i.e., $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{46}Ca_{\#2}/^{44}Ca_{\#2}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$) and measuring ^{40}Ca, ^{44}Ca, and ^{44}Ca, and ^{46}Ca and ^{48}Ca in the first and second lines, respectively. By contrast, improper selection of cup configuration and ratio combination can sharply decrease the predicted internal precision of δ^{44}Ca. For example, B_1, D_2 and C_3 combination decreased the internal precision by 25%, 20%, and 25%, respectively, compared to that obtained using optimum combination of C_1, A_2 and D_3. Moreover, as shown in Figure 2-C_3, the optimum area (optimum ranges of composition of double spike and proportion of double spike in the mixture) changes significantly when improper selection of cup configurations and ratio combinations is made.

It is clear from the above results that the selection of cup configuration and ratio combination has a significant impact on the predicted precision of δ^{44}Ca. The large difference in the predicted internal precision between simulations under peak jump and under static collection mode suggests that the additional uncertainties arising from IMVs not only reduce the precision of δ^{44}Ca, but also have complex effects on uncertainty propagation. Moreover, the combinations of IMVs have a significant impact on the predicted internal precision of δ^{44}Ca, even with use of the same group of standard

uncertainties. Thus, all possible cup configurations, ratio combinations, and IMVs used to construct ratios should be fully investigated under the actual analysis conditions, such as the number of Faraday cups, peak jump lines and mass dispersion of isotopes. Based on Monte Carlo prediction, the optimum IMVs of Ca isotopes to generate three Ca ratios can be identified, resulting in significant improvements on the predicted precision of δ^{44}Ca.

Effect of integration time

Compared to static collection mode, peak jump mode brings in variable Δt_i in different lines. Independent variation of integration times on each line also has an impact on the precision. With the proposed Monte Carlo method, internal precision was predicted by changing integration time of line1 (Δt_1) and line2 (Δt_2), separately, under A_1-D_1 combinations for ^{42}Ca-^{48}Ca double spike, while keeping a fixed total integration time (Δt) of 16s (Fig. 3a). Predicted internal precision of δ^{44}Ca showed a significant variation with use of independent Δt_1 and Δt_2, compared to that use of $\Delta t_1 = \Delta t_2$ under fixed total Δt. As shown in Fig. 3a, the optimum cup configuration and ratio combination (C_1) predicted above (with use of $\Delta t_1 = \Delta t_2$=8s) generated the most precise results compared to A_1, B_1 and D_1 conditions, while each condition using optimal Δt_1 and Δt_2, respectively. Therefore, the optimum cup configuration and ratio combination is a robust choice under both equal and independent integration times for different lines with use of ^{42}Ca-^{48}Ca double spike, and this is also true for ^{43}Ca-^{48}Ca and ^{46}Ca-^{48}Ca double spikes.

Furthermore, the relationship between predicted internal precision and independent Δt_1

and Δt_2 can be used to reduce the difference of ion count per sample in different lines. For example, ^{40}Ca is about 40 times more abundant than ^{44}Ca, and 20 times more abundant than ^{48}Ca in spiked samples with use of optimal ^{42}Ca-^{48}Ca double spike. In the case of similar predicted internal precision, using Δt_1 =4 and Δt_2=12, respectively can narrow this gap by 3 times compared to using Δt_1 =Δt_2=8 under C_1 configuration. Total integration times of 16s were experimentally tested using Δt_1 =4 and Δt_2=12 (Fig. 3a). It is evident that experimental results lie fairly close to the predicted curve, confirming the feasibility of Monte Carlo method for the internal precision estimation with use of independent integration time in different lines.

On the other hand, peak jump mode is a time-consuming method relative to static mode. The uncertainty model indicates that the uncertainty of signal intensity of each isotope is largely dependent on the integration time. Conceptually, the longer the integration time, the more precise the results. As shown in Fig. 3b, for ^{42}Ca-^{48}Ca double spike with A1-E1configurations, the predicted internal precisions of δ^{44}Ca increase significantly as total integration time increases from 2s to 16s, and then only slightly increase at higher integration times. Unfortunately, integration time is a major limitation for high sample throughput analysis since the sample heating procedure is relatively constant. Analysis time is doubled when peak jump collection mode is applied. Total integration time of 16s (Δt_1 = Δt_2=8) was chosen to achieve high precision Ca isotope ratio measurements while maintaining relatively high sample throughput in this study.

Validation of Monte Carlo prediction

NIST SRM 915a and NIST SRM 915b standard solutions were spiked with ^{42}Ca-^{48}Ca double spike for the δ^{44}Ca measurements to validate Mont Carlo method for precision prediction. The ^{42}Ca-^{48}Ca double spike was prepared from two single spikes of ^{42}Ca (94.49%) and ^{48}Ca (97.80%) (Table 1). Since the difference between the real and the pure (100%) single spikes in predicted results was smaller than the accuracy of Mote Carlo technique under 5000 simulations, the composition of double spike and the proportion of double spike in the mixture were prepared following the optimal predicted results (Fig. 2 C_1). The composition of the ^{42}Ca-^{48}Ca double spike was calibrated against the NIST 915a by subtracting the standard from the mixture using a reverse process that calculates sample compositions. Thus, all the δ^{44}Ca reported in this paper were relative to NIST SRM 915a. These two spiked standard solutions were directly analyzed without chemical separation process. Therefore, uncertainty sources were limited in instrumental analysis process. The ion beams of ^{42}Ca and ^{44}Ca were collected in every line to simulate all the potential cup configurations (A_1-D_1) under two lines measurement (Table 2). Total of 81 data points were obtained with each data point representing the result of a single run session of 100 scans (10 blocks × 10 cycles). Internal precision and external precision from these data were then compared with the results predicted using Monte Carlo simulation.

Results of measured internal precision ($2\sigma_{SEM}$) of δ^{44}Ca using different Ca ratio

combinations are presented in Fig. 4. Overall, observed and predicted internal precision are in good agreement, but 10-17 data points showed irregular fractionation trends during measurements, mainly due to a poor sample loading process wherein sample was spread on the filament and resulted in erratic patterns of fractionation[16, 20, 21] as shown in Fig. 4e. Sample loading has a significant contribution to the measured internal precision of $\delta^{44}Ca$ regardless of cup configuration and ratio combination. However, the best internal precision can be obtained using the predicted optimum condition (C_1) in nearly all data points. By removing the data points due to poor sample loading, measured internal precision of $\delta^{44}Ca$ under different ratio combinations of ^{42}Ca-^{48}Ca double spike measurements are in good agreement with the predicted internal precision, confirming the accuracy of the proposed Monte Carlo simulation method accounting for errors from Johnson noise and counting statistics. Therefore, high precision measurements can only be obtained by rigorous sample loading protocol as well as selecting optimum ratio combination and double spike pair. Poor data points with the erratic fractionation trends (with a feature of internal precision >0.03‰) can be easily identified during off-line data reduction process and be rejected. The fluctuations of observed internal precision around the predicted lines indicate the slight deviation of intensity of ^{40}Ca from 9 V during data acquisition.

The long-term reproducibility of $\delta^{44}Ca$ for four months measurements under A_1-D_1 combinations were found to be 0.23‰, 0.21‰, 0.21‰, 0.23‰ ($2\sigma_{SD}$, n = 50) and 0.20‰, 0.17‰, 0.17‰, 0.20‰ ($2\sigma_{SD}$, n = 18) for NIST SRM 915a and NIST SRM 915b,

respectively. Using the optimum condition (C_1) produced the best external precisions for both NIST SRM 915a and NIST SRM 915b, even though the sequence of observed external precision deviated from the predicted order ($B_1>A_1=D_1>C_1$). However, the external reproducibility was found to be 9 and 10 times worse than the internal precision, indicating additional uncertainty sources (e.g., filament shape, sample loading, focusing and faraday cup poison) other than Johnson noise and counting statistics. This poor agreement between internal and external precision was also reported in previous studies.[1,20,22] Recent research[22] suggested that filament reservoir mixing effect was responsible for this big differences between measured internal precision and external precision. The Montel Carlo simulation method cannot be used to predict the external reproducibility in this case, since these additional uncertainty sources cannot be quantified. However, certain uncertainty can be reduced by correction. Lehn *et al*.[9] and Schmitt *et al*.[23] reported an instrumental drift occurring between sessions, resulting in a systematic offset of δ^{44}Ca. This systematic offset in δ^{44}Ca is caused by Faraday cup deterioration (also called cup poison) in the instrument.[9, 16, 23] In our results, a similar instrument drift was observed in δ^{44}Ca value evaluated by all ratio combinations (A_1-D_1). Take the results with use of C_1 combination for example, as shown in Fig. 5, a systematic offset (~+ 0.16‰) in δ^{44}Ca value of NIST SRM 915a was found at the end of July and accompanied by a similar shift in the results of NIST SRM 915b. For this reason, the "offset correction" proposed by Lehn *et al.*[9] was applied to both NIST SRM 915a and NIST SRM 915b by subtracting the same offset factor (+0.16‰) from

the draft period. After the correction, mean values of 0.00 ± 0.15 (2 σ_{SD}, n=50) and 0.71 ± 0.11(2 σ_{SD}, n=18) were obtained for δ^{44}Ca relative to NIST SRM 915a for NIST SRM 915a and NIST 915b, respectively, with use of C_1 combination. The corrected results showed a two-fold improvement compared to that of the uncorrected data. The mean value of NIST SRM 915b using C_1 ratio combination agrees well with the published values of ~0.72‰,[9, 24] confirming the accuracy of the proposed correction method. Given that the drifts in results were similar for all ratio combinations, the external precisions can be improved in the same scale.

Overall, the observed precisions (both internal and external) can be accurately predicted only when all the potential uncertainty sources are considered. Here, the difference between the observed and predicted precisions suggests that there are other uncertainty sources besides Johnson noises and counting statistics. However, optimum measurement conditions (cup configuration and ratio combination), predicted by counting IMVs effect using Monte Carlo simulation technique which simulates uncertainties from Johnson noises and counting statistics, always give most precise results for both internal and external precisions. This may be due to the fact that optimum measurement conditions were based on the IMVs effect, and the IMVs were measured in different peak jump lines from the same ion beam at nearly the same time (neglect the small variation of beam intensity between different lines). The fluctuation of ion beam during different scans between one analysis session and another session causes the deviation of observed internal and external

precisions from those of predicted, respectively, but it does not affect the optimum condition which is determined by IMVs effect. Clearly, whenever the IMVs occurs, the optimum condition can be determined by using the Mote Carlo technique. However, uncertainties occurred during data collection procedure, such as unequal collector and/or gain efficiency during collection, may impact this optimum condition.

According to the previous studies, Mote Carlo technique which simulates uncertainty from Johnson noises and counting statistics has been successfully applied to predict experimental precision, e.g., for δ^{49}Ti,[25] δ^{56}Fe,[7, 8, 26] δ^{66}Zn,[8] and δ^{114}Cd,[8, 27] under static collection mode using MC-ICPMS. It can thus be inferred that the proposed Mote Carlo model can be used as a powerful predetermination of optimum measurement conditions for all non-stable isotopes measured by DS-TIMS or DS-MC-ICPMS under peak jump collection mode.

Conclusions

This study presents an efficient model for theoretically predicting the internal precision of double spike technique when peak jump mode is employed, using Monte Carlo simulation technique in considering uncertainty contributions from Johnson noise and counting statistics. The model was assessed by the investigation of three different double spike pairs of ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca, and ^{46}Ca-^{48}Ca which commonly cannot be measured in static collection mode. Predicted results show 25%, 20%, and 25% improvements by using

optimum cup configurations and ratio combinations for $\delta^{44}Ca$ with use of ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca, and ^{46}Ca-^{48}Ca double spike, respectively. Observed results from repeat measurements of NIST SRM 915a and NIST SRM 915b confirm the feasibility of the proposed model for predicting optimal cup configuration and ratio combination. Long-term reproducibility can be further improved if a rigorous analysis condition protocol is available since extra error source has a significant impact to the external precision of $\delta^{44}Ca$.

As demonstrated for Ca isotope measurements, Monte Carlo simulation is a useful tool in achieving accurate and precise results because of the following reasons: 1) optimal double spike predicted by using static collection mode is also suitable for peak jump collection mode; 2) it provides a clear and simple selection of cup configuration in each line when peak jump mode is used; 3) measurement precision can be improved by using optimal ratio combination during data reduction when all IMVs are obtained; 4) difference in ion count per sample caused by difference in isotope abundances can be reduced by using appropriate integration times in different lines, while maintaining good measurement precision. The proposed method is expected to be applicable to other isotopes which cannot be measured simultaneously in a single line using double spike technique.

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Table 1. Isotopic abundance (%) of spikes and reference material.

Material	^{40}Ca	^{42}Ca	^{44}Ca	^{48}Ca
^{42}Ca single spike	0.004	94.49	0.04	0.02
^{48}Ca single spike	0.001	0.01	0.001	97.80
^{42}Ca-^{48}Ca double spike [a]	4.04	41.90	0.43	53.43
NIST SRM 915a [b]	98.89	0.64	2.06	0.18

[a] Calibrated composition. [b] Taken from Russell *et al.*[15]

Table 2. TIMS operating conditions

Instrument parameter	Setting
Cup configuration	Line 1: ^{39}K (L3), ^{40}Ca (L2), ^{42}Ca (C), ^{43}Ca (H1), ^{44}Ca (H2) Line 2: ^{42}Ca (L3), ^{44}Ca (L1), 45.50 (C), ^{48}Ca (H3)
Resistors	$10^{11}\Omega$ for all amplifiers
Intensity	^{40}Ca about 9 V within 10% variation
Integration time	8 s in each line
Idle time	4 s after each line
Blocks number	5
Cycles number	20
Baseline	before each block
Focus	warm-up and every 2 blocks
peak center	warm-up and every 2 blocks
Amplifier rotation	After each block
Sample heating program	**Setting**
Step 1: ION filament[a]	1000 mA/min to 1420 °C
Step 2: EVPA filament[b]	250 mA/min to 1500 mA
Step 3: EVPA filament	60 mA/min to 1650 mA
Step 4: EVPA filament	Waite for 5 min, focus
Step 5: EVPA filament	Open valve, 60 mA/min to 4000 mV (pilot mass ^{40}Ca)
Step 6: EVPA filament	30 mA/min to 7000 mV (pilot mass ^{40}Ca), focus
Step 7: EVPA filament	10 mA/min to 9000 mV (pilot mass ^{40}Ca), focus
Step 8: Start data evaluation	

[a] ION filament = ionization filament. [b] EVAP filament = evaporation filament

Figure captions

Fig. 1 Schematic diagram of theoretically possible cup configurations for Ca isotope ratio measurements with use of ^{42}Ca-^{48}Ca, ^{43}Ca-^{48}Ca, ^{46}Ca-^{48}Ca double spikes. Configuration (a) and (b) measure ^{42}Ca or ^{43}Ca or ^{46}Ca in both lines, but measure ^{44}Ca in a different line. Configuration (c) and (d) measure ^{44}Ca in both lines, but measure ^{42}Ca or ^{43}Ca or ^{46}Ca in a different line. Configuration (e) measures all isotopes in one line. Dashed cups represent the case with use of ^{43}Ca-^{48}Ca, and ^{46}Ca-^{48}Ca double spike, respectively.

Fig. 2 Monte Carlo estimation of the internal precision ($2\sigma_{SEM}$) of δ^{44}Ca arising from various double spike pairs, proportion of primary spike in double spike and proportion of double spike in mixture and use of different ratio combinations. Each ratio combination is corresponding to one cup configuration presented in Fig. 1. A_1-A_3: $^{40}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{44}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{48}Ca_{\#2}/^{4i}Ca_{\#2}$ (i = 2, 3 or 6). B_1-B_3: $^{40}Ca_{\#1}/^{4i}Ca_{\#1}$, $^{44}Ca_{\#2}/^{4i}Ca_{\#2}$, $^{48}Ca_{\#2}/^{4i}Ca_{\#2}$. C_1-C_3: $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#1}/^{44}Ca_{\#1}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$. D_1-D_3: $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#2}/^{44}Ca_{\#2}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$. E_1-E_3: $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{4i}Ca_{\#1}/^{44}Ca_{\#1}$, $^{48}Ca_{\#1}/^{44}Ca_{\#1}$. The subscript numbers (e.g., A_1) denote the double spike pairs: 1 = ^{42}Ca-^{48}Ca; 2 = ^{43}Ca-^{48}Ca; 3 = ^{46}Ca-^{48}Ca. The total intensity and individual integration time for each line used for Monte Carlo estimation were 10 V and 8 s, respectively. The abundances of primary spikes used in the calculation were all assumed to be 100% enriched. Only predicted internal precision within 0.060‰ is

shown in the contour plots. The filled circle marks the optimal ^{42}Ca-^{48}Ca double spike composition tested in this study (q=$^{42}Ca/(^{42}Ca+^{48}Ca)$=0.44, p=double spike/mixture=0.12)

Fig. 3 The effect of integration time on predicted internal precision ($2\sigma_{SEM}$) of $\delta^{44}Ca$ under different cup configurations and ratio combinations. Internal precision is predicted by Monte Carlo simulation with total intensity of 10V and use of an optimum ^{42}Ca-^{48}Ca double spike. Integration time in line one (Δt_1) and line two (Δt_2) are allowed to vary independently, while keeping a constant total integration time (Δt) of 16s (a). Total integration time varies from 2s to 16s, while integration time in line one and line two are set equal (b).

Fig. 4 Comparison of observed and predicted internal precision of $\delta^{44}Ca$ under different ratio combinations. Data points are composed by 61 measurement results of NIST SRM 915a (white area) and 21 measurement results of NIST SRM 915b (grey area). Observed values calculated by using ratio combination $^{40}Ca_{\#1}/^{42}Ca_{\#1}$, $^{44}Ca_{\#1}/^{42}Ca_{\#1}$, $^{48}Ca_{\#2}/^{42}Ca_{\#2}$ (a); $^{40}Ca_{\#1}/^{42}Ca_{\#1}$, $^{44}Ca_{\#2}/^{42}Ca_{\#2}$, $^{48}Ca_{\#2}/^{42}Ca_{\#2}$ (b); $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{42}Ca_{\#1}/^{44}Ca_{\#1}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$ (c); and $^{40}Ca_{\#1}/^{44}Ca_{\#1}$, $^{42}Ca_{\#2}/^{44}Ca_{\#2}$, $^{48}Ca_{\#2}/^{44}Ca_{\#2}$ (d). The open symbols represent samples that had an erratic pattern of fractionation trend during the TIMS measurements. Inserted figures (e) and (f) depict typical fractionation trends (presented by variation of $^{42}Ca/^{48}Ca$ ratio during 100 scans) of bad and good sample-loading results, respectively. Solid lines indicate the predicted internal precision, while dash lines represent the mean value of all the observed internal precision.

Fig. 5 Four month measurements of $\delta^{44}Ca$ in NIST SRM 915a and SRM 915b. Data points which show an erratic pattern of fractionation trend were rejected during off-line data reduction. In (a) data points are presented without offset correction, while in (b) have been applied with offset correction. The red line is the reference values 0.72‰[9, 24] of $\delta^{44}Ca$ in NIST SRM 915b. Error bars are $2\sigma_{SEM}$.

Figure 1

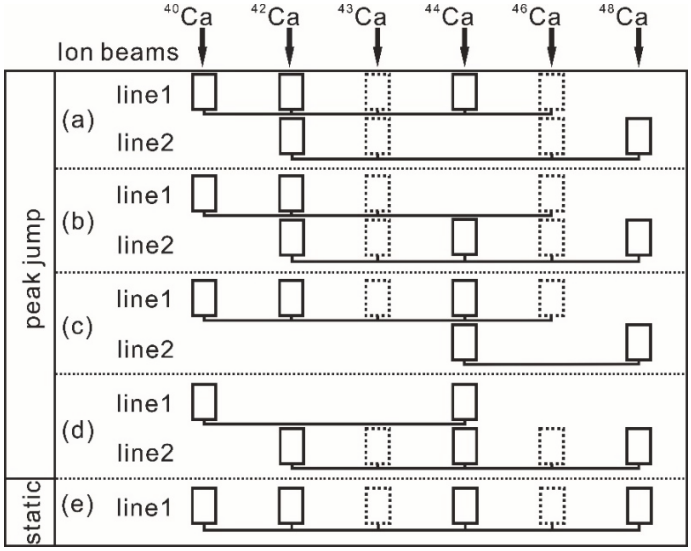


Figure 2

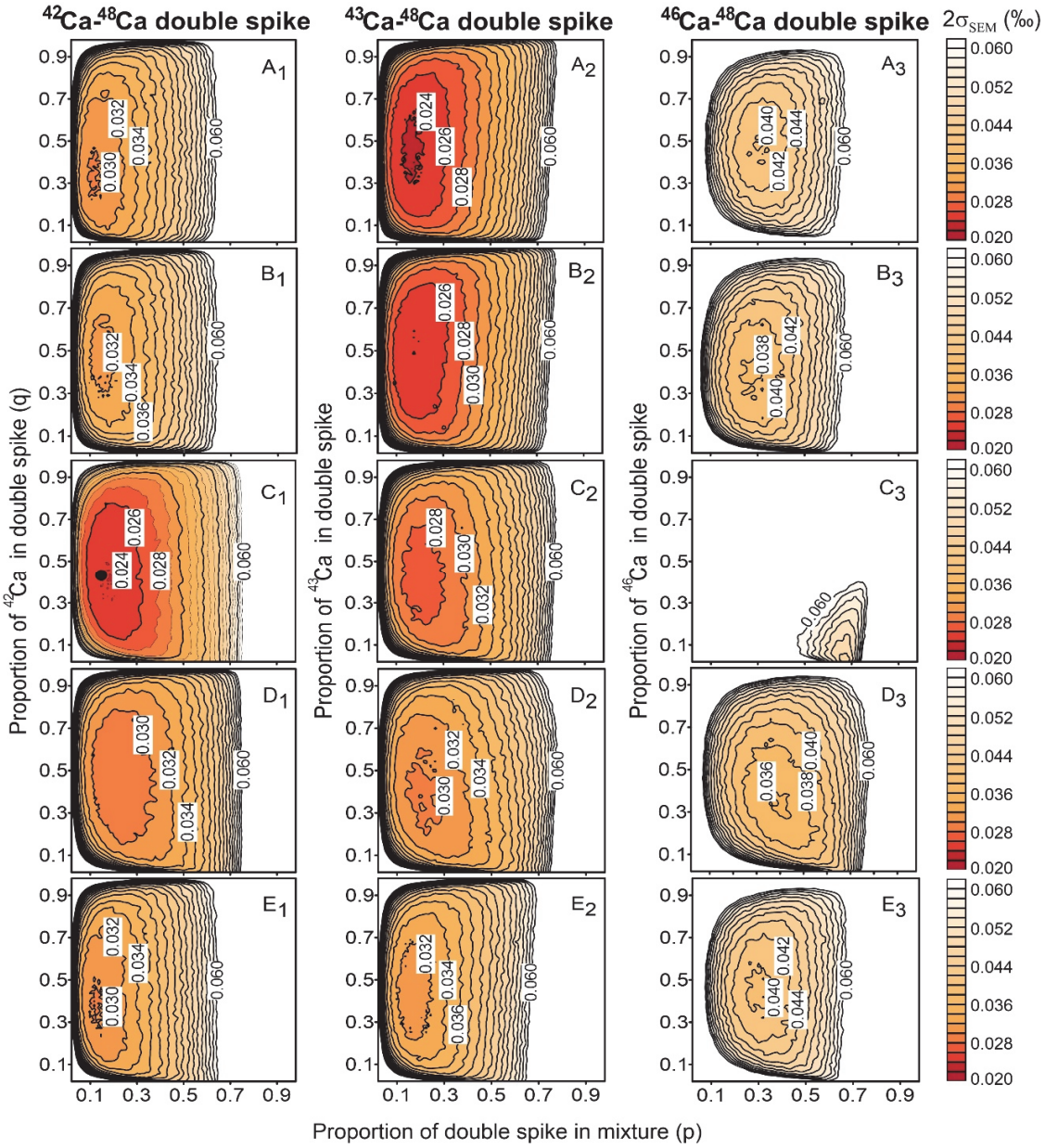
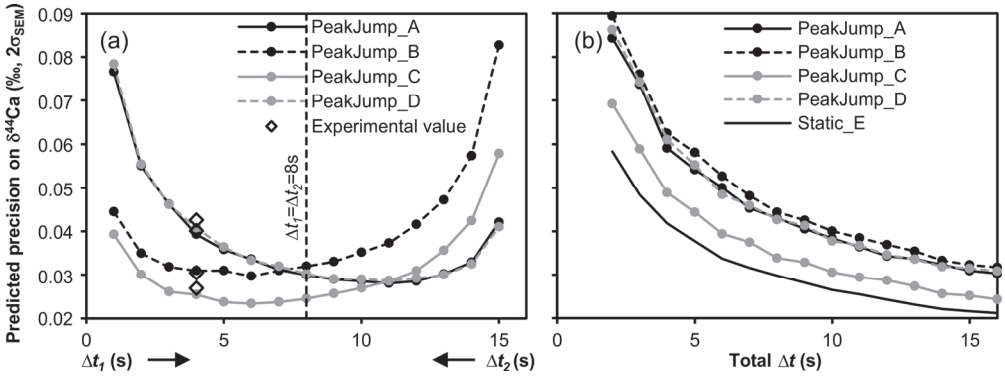


Figure 3



552 **Figure 4**

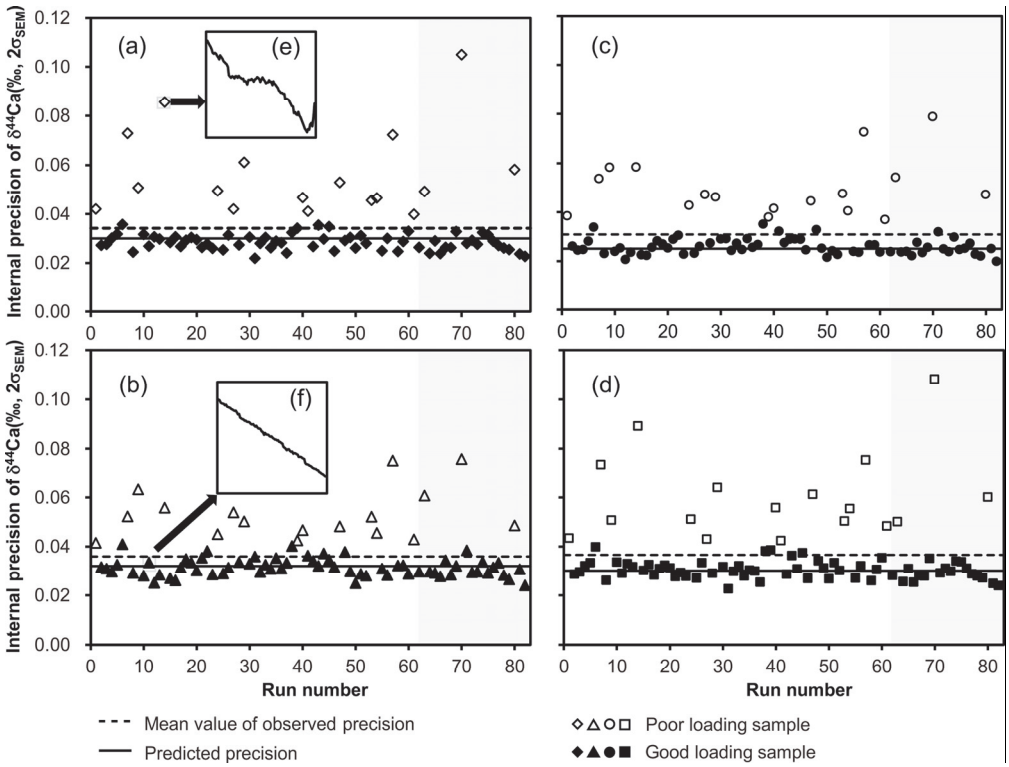


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Figure 5