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A "peak cut" procedure of column separation for calcium isotope measurement using the double spike technique and thermal ionization mass spectrometry (TIMS)

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Full recovery from column separation and matrix effects are the two factors that need to be considered for the high-precision analysis of stable Ca isotopes, but generally they are difficult to balance. In many cases, to get a pure Ca fraction, the interference of the matrix elements is reduced at the cost of discarding a fraction of Ca overlapping with other elements (*e.g.* Sr and K). However, quantitative evaluation using this approach is challenging but greatly needed. Our study investigates the influence of low Ca recovery on $\delta^{44/40}$Ca using thermal ionization mass spectrometry (TIMS) with the double spike technique. $\delta^{44/40}$Ca of IAPSO seawater, ML3B-G and BHVO-2 in different Ca subcuts (*e.g.* 0–20, 20–40, 40–60, 60–80 and 80–100%), display limited variation after iterative correction by ^{42}Ca–^{43}Ca double spike with the exponential law. Notably, $\delta^{44/40}$Ca of each Ca subcut with ~20% recovery is consistent with that of the Ca cut with full recovery, within a margin of error. Our results indicate that ^{42}Ca–^{43}Ca double spike technique can simultaneously correct Ca isotopic fractionation, occurring during column separation, and TIMS determination, because both follow the exponential fractionation law well. Therefore, a "peak cut" procedure of column separation for Ca isotope measurement using the double spike technique on TIMS is proposed. Briefly, we can mix the double spike with the sample solution well before column separation, then collect the peak of the Ca cut and abandon both sides of the Ca eluate that may overlap with other elements. This procedure would eliminate matrix effects efficiently, especially for samples with low CaO contents which typically must be passed through the column twice (*e.g.* peridotite and dunite).

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1 Introduction

As one of the most abundant elements in the Earth, Ca plays an important role in geological and biological processes.[1,2] It has six "stable" isotopes of ^{40}Ca (96.941%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%) and ^{48}Ca (0.187%).[1,2] Because of the large relative mass difference ($\Delta m/m$ = 20%) between the heaviest and lightest isotopes, large Ca isotopic fractionation (~6‰) has been observed in nature.[1–3] Thus, Ca isotopes have been widely applied as an effective geochemical tracer in many different processes, such as determining the origin of rocky plants,[4–8] tracing recycled marine carbonates,[9,10] observing mantle heterogeneity[11–14] and investigating oceanic calcium cycling.[15,16]

High-precision isotope measurements for Ca are difficult because of (1) the large difference in the natural abundance of Ca isotopes, with ^{40}Ca dominating the system, (2) significant Ca isotopic fractionation during analysis, and (3) isobaric interference from elemental and molecular isobars during mass determination (*e.g.* ^{40}K$^+$, ^{48}Ti$^+$, ^{88}Sr^{2+}, ^{24}Mg^{16}O$^+$ and ^{27}Al^{16}O$^+$). The counting statistics of the low intensity ion beam for the minor nuclides could influence the measurement uncertainty during the analyses. To obtain precise measurements, high intensity ion beams are required for the low abundance of Ca isotopes. In the current generation of instruments, the maximum measurable signal in the amplifiers of the mass spectrometer is 55 V. The counting of the minor nuclides is limited by the size of the ^{40}Ca beam.[2] Recently, it has become possible to change the amplifier resistance, which can increase the counting statistics and provide a high intensity of the minor nuclides.[2]

Because of the large relative mass difference, large Ca isotopic fractionation would occur during chemical purification and mass determination. This hindered the improvement of high-precision measurements of Ca isotopes for the first few years,[17–19] until 1978, when Russell *et al.*[20] firstly observed mass-dependent Ca isotopic fractionation in nature with a $\delta^{44/40}$Ca resolution of 0.5‰ using TIMS with the ^{42}Ca–^{48}Ca double spike

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technique. Instrumental mass fractionation was corrected by a mass-dependent law.[20] Afterwards, ^{42}Ca–^{43}Ca and ^{43}Ca–^{48}Ca double spikes were also applied to Ca isotope analysis.[21–25] In addition, a non-trivial number of studies have used multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for Ca isotope determination.[26–28] Generally, the standard-sample bracketing (SSB) method was applied to correct instrumental fractionation.[27]

To eliminate isobaric interference on the Ca isotope system, samples are purified through ion-exchange column separation before analysis. In particular, rock samples or minerals with low CaO contents (*e.g.* peridotite, orthopyroxene and olivine) usually are subjected to column separation twice.[11,12,29] Based on the fact that significant Ca isotopic fractionation occurs during this process,[30,31] full recovery during column separation is greatly needed, otherwise an incorrect value would result from the poor recovery.[31] However, matrix effects could be induced when full recovery is achieved, as other elements that might overlap with the Ca cut during column separation are also collected and cause isobaric interference.[25,26] Thus, full recovery and low matrix effects, which are considered to be the two important factors affecting the true value, are difficult to be obtained simultaneously. Both of them need to be considered, especially for MC-ICP-MS measurements with the SSB method, which can only correct instrumental fractionation.[29,31,32] This is why Wieser *et al.*[26] only left <1% of the Ca tail that overlapped the onset of the Sr peak during Ca purification.

However, the Ca recovery is not considered to be a significant issue for TIMS determination with the double spike technique. For example, Amini *et al.*[23] generously cut the Ca peak tails on both sides of the chromatograms and collected a fairly pure Ca eluate in particular for the ultramafic samples that are high in Mg, so that the Ca yield was diminished to about 80%. Cenki-Tok *et al.*[33] truncated the Ca cut with a recovery yield of about 70% to eliminate isobaric interferences caused by the presence of K, Mg and Sr. Mondal and Chakrabarti[29] achieved a Ca yield of between 80 and 90% after performing ion-exchange chromatography twice for better purification. Even so, until now, whether Ca isotopic fractionation during column separation caused by poor recovery can be corrected by the double spike technique has been poorly understood.

In this study, we measure Ca isotopic compositions of each ~20% Ca subcut of three reference materials on TIMS to check whether poor recovery has an effect on $\delta^{44/40}Ca$ after correction by the double spike technique. $\delta^{44/40}Ca$ in all of the Ca subcuts displays limited variation and is consistent with that of the Ca cut with full recovery, within a margin of error. Our results suggest that even though the Ca recovery is decreased to ~20%, the Ca isotopic fractionation that occurred during column separation would be corrected along with instrumental mass fractionation with the double spike technique. Therefore, we propose a "Ca peak cut" procedure of column separation using the double spike technique on TIMS, which would separate Ca from the other matrix efficiently for matrix-complicated samples.

2 Experimental methods

Three reference materials were selected for the experiments, including IAPSO seawater, ML3B-G glass (from MPI-DING) and BHVO-2 (from USGS). NIST SRM 915a was also analyzed as a reference material. Analysis of the Ca isotopes, including column separation and mass determination, was carried out at the State Key Laboratory of Isotope Geochemistry (SKLaBIG), Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). The detailed analytical procedures provided below are similar to those in previous publications.[31,34]

2.1 Sample preparation

The ML3B-G glass was firstly ground into a 200 mesh power in an agate mortar. About 30 mg of the sample powers of ML3B-G and BHVO-2 were then dissolved using a 3 : 1 mixture of concentrated HF and HNO_3 in 7 ml Savillex beakers on a hotplate at 120 °C for 7 days. The sample solutions were evaporated to dryness at 100 °C then dried down several times with 6 M HCl to ensure complete digestion. The samples were finally dissolved in 1.6 M HCl for column separation.

About 3 ml IAPSO seawater was dried down in a 7 ml Savillex beaker at 100 °C. To convert the cations into chloride form, this sample was evaporated to dryness several times with concentrated HCl. Finally, the IAPSO seawater was dissolved in 1.6 M HCl for column separation.

About 5 mg NIST SRM 915a was directly dissolved in 10% v/v HNO_3. An aliquot containing 50 μg Ca was mixed with an appropriate amount of ^{42}Ca–^{43}Ca double spike solution (containing 8 μg Ca) to obtain the sample/spike ratio of $^{40}Ca_{sample} : {}^{42}Ca_{spike} = 7$.[35] Detailed information for the ^{42}Ca–^{43}Ca double spike solution was reported by Liu *et al.*[34] The samples were then dried down and re-dissolved in 10 μl of 10% v/v HNO_3 for TIMS determination without column separation.

2.2 Column separation

Calcium was purified using 1 ml Bio-Rad AG MP-50 (100–200 mesh) resin packed in a PTFE micro-column. To separate the purified Ca cut into five parts with a recovery yield of about 20%, a Ca elution curve must be calibrated. As the chemical procedure for separating Ca established at our laboratory does not change with the lithology,[36,37] we only took a sample of BHVO-2 for calibration. An aliquot of BHVO-2 containing 58 μg Ca was loaded onto the pre-conditioned column and eluted with 1.6 M HCl. The eluate was continuously collected for every 1 ml of 1.6 M HCl. The Ca elution curve was then calibrated by analyzing each of the 1 ml elutions with ICP-AES (Fig. 1).

An aliquot of the sample solution (IAPSO seawater, ML3B-G and BHVO-2) containing 50 μg Ca was mixed with an appropriate amount of ^{42}Ca–^{43}Ca double spike solution (containing 8 μg Ca). The mixture solutions were dried down and treated with concentrated HCl several times. They were then re-dissolved in 0.05 ml of 1.6 M HCl and loaded onto the pre-conditioned columns for column separation. Based on the calibrated Ca elution curve, five equal fractions of purified Ca were obtained (Fig. 1). Briefly, 17 ml of 1.6 M HCl was used to elute most of the

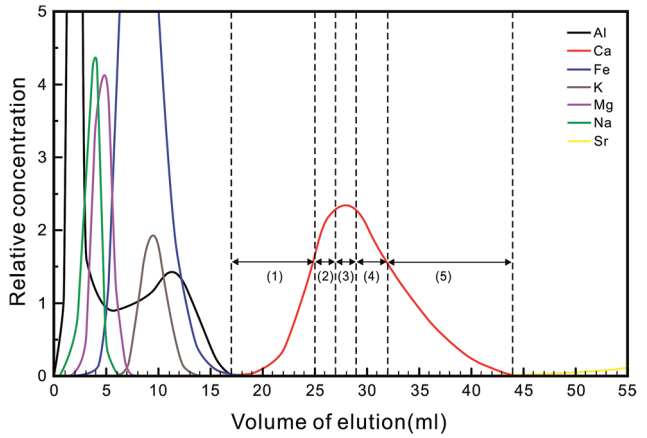

Fig. 1 The Ca elution curve of BHVO-2 passed through 1 ml Bio-Rad AG MP-50 (100–200 mesh) resin packed in a PTFE micro-column. Based on the relative concentration of Ca in each 1 ml eluate, the Ca cut was divided into five subcuts with Ca recovery yields of about 20% (defined as (1), (2), (3), (4) and (5), respectively).

matrix, including Al, K, Na, K and Fe. Five equal Ca subcuts (defined as (1), (2), (3), (4) and (5)) were then obtained by eluting 8 ml, 2 ml, 2 ml, 3 ml and 12 ml of 1.6 M HCl sequentially. These Ca subcuts were then dried down and treated with concentrated HNO_3 several times. Finally, they were re-dissolved in 10% v/v HNO_3 for TIMS determination.

For comparison, another aliquot of IAPSO seawater, ML3B-G and BHVO-2 mixed with the ^{42}Ca–^{43}Ca double spike was also loaded onto the columns for column separation. The purified Ca cuts were collected as a whole this time, so that the recovery yield was about 100% (full recovery). These purified Ca cuts were then treated following the procedure described above for TIMS determination. During column separation, at least one blank was processed with the samples to monitor the blank of each batch purification.

2.3 TIMS measurements

Calcium isotopes were measured on a ThermoTriton™ TIMS. About 5 μg of purified Ca dissolved in 1 μl of 10% v/v HNO_3 was directly loaded onto the out-gassed 99.995% Ta filament and dried at a filament current of 0.8 A. A droplet of 1 μl 10% v/v H_3PO_4 was loaded on the sample spot as an activator. After the activator was dried down, it was then heated at 1.5 A and 2.2 A for 1 minute, respectively. The filament was taken to dull red at ~2.8 A and retained for 10 seconds. Finally, the current was slowly reduced to zero.

The instrument was operated in positive mode, and two analytical sequences of cup configuration were adopted as reported in previous publications.[31,34] Mass 41 was measured to monitor the isobaric interference of ^{40}K on ^{40}Ca using $^{40}K/^{41}K = 1.7384 \times 10^{-3}$.[21,31] The ^{42}Ca–^{43}Ca double spike technique was used to correct instrumental fractionation through an iterative algorithm with an exponential law similar to Heuser *et al.*[21] and Holmden.[38] All Ca isotopic data are reported as $\delta^{44/40}Ca$ relative to NIST SRM 915a, which is defined as $\delta^{44/40}Ca = [(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{SRM\ 915a} - 1] \times 1000$. Because of the limited Ca amount, each Ca subcut with ~20% Ca recovery was measured only once and the internal precision is reported as the analytical uncertainty. Other Ca cuts with full recovery were measured ≥4 times and the two standard deviations (2SD) are reported as the analytical uncertainty. The long-term whole procedural Ca blanks ranged from 20 to 70 ng, which were generally negligible compared to 50 μg Ca loaded onto the column. The long-term external reproducibility of the $\delta^{44/40}Ca$ value of NIST SRM 915a is 0.01 ± 0.11‰ (2SD, $n = 233$).

3 Results

The $\delta^{44/40}Ca$ values of each Ca subcut with ~20% recovery and the Ca cut with full recovery for IAPSO seawater, ML3B-G and BHVO-2 are listed in Table 1. $\delta^{44/40}Ca$ of the first 20% Ca subcut of BHVO-2 was not obtained, as the filament was broken during TIMS determination (Table 1). The $\delta^{44/40}Ca$ values of the Ca cut with full recovery for IAPSO seawater, ML3B-G and BHVO-2 are 1.83 ± 0.11‰ (2SD, $n = 12$), 0.79 ± 0.10‰ (2SD, $n = 8$) and 0.82 ± 0.11‰ (2SD, $n = 12$), respectively, which are in excellent accordance with the results reported in previous publications.[6,23–25,34,39–41] For the samples of IAPSO seawater, ML3B-G and BHVO-2, the $\delta^{44/40}Ca$ values of all five Ca subcuts with ~20% recovery exhibit limited variation after correction by the ^{42}Ca–^{43}Ca double spike with the exponential law. Importantly, $\delta^{44/40}Ca$ of each Ca subcut is in agreement with $\delta^{44/40}Ca$ of the Ca cut with full recovery, within a margin of error (Fig. 2).

4 Discussion

4.1 The limited effect of poor recovery on $\delta^{44/40}Ca$ using the double spike technique

As for many different isotopic systems including Mg, Fe, Sr and Nd, significant isotopic fractionation usually occurs during column separation.[42–46] Similarly, significant Ca isotopic fractionation (~4‰) was also observed during this process.[31] Light Ca isotopes were held more strongly by the Bio-Rad AG MP-50 (100–200 mesh) resin and tend to be enriched in the tail fraction of the Ca cut elution,[31] which behaved similar to that of the Dowex 50W-X8 (200–400 mesh) resin.[30] Therefore, if this Ca isotopic fractionation during column separation cannot be corrected appropriately, it will have a serious effect on the accuracy of $\delta^{44/40}Ca$, especially for MC-ICP-MS measurements with the SSB method. Zhu *et al.*[31] calculated the uncertainties caused by poor recovery during column separation, showing that a 3% loss from the end of the elution could lead to a 0.05‰ deviation from the reference value, while a 2% loss from the beginning could cause a 0.07‰ deviation.[31]

Although light Ca isotopes prefer to be enriched in a later elution of the Ca cut than the heavy ones during column separation, $\delta^{44/40}Ca$ of all five Ca subcuts with only about 20% recovery were not decreased with elution after correction by the ^{42}Ca–^{43}Ca double spike technique in this study (Fig. 2). Importantly, they displayed quite limited variation and are all in accordance with $\delta^{44/40}Ca$ of the Ca cut with full recovery (Fig. 2) and previous studies, within a margin of error.[6,23–25,34,39–41] These results suggest that the large Ca isotopic fractionation (~4‰)

Table 1 $\delta^{44/40}$Ca of each Ca subcut with ~20% recovery and the Ca cut with full recovery for IAPSO seawater, ML3B-G, BHVO-2 and NIST SRM 915a

	$\delta^{44/40}$Ca of each Ca subcut with ~20% recovery[a]					
	(1) 0–20%	(2) 21–40%	(3) 41–60%	(4) 61–80%	(5) 81–100%	$\delta^{44/40}$Ca of Ca cut with full recovery[b]
Seawater	1.77 ± 0.06	1.87 ± 0.06	1.86 ± 0.06	1.88 ± 0.07	1.81 ± 0.06	1.83 ± 0.11
ML3B-G	0.86 ± 0.07	0.78 ± 0.07	0.79 ± 0.08	0.85 ± 0.08	0.84 ± 0.08	0.79 ± 0.10
BHVO-2	—[c]	0.84 ± 0.07	0.84 ± 0.08	0.83 ± 0.07	0.81 ± 0.07	0.82 ± 0.11
NIST SRM 915a	—	—	—	—	—	0.01 ± 0.11

[a] The analytical uncertainty of the results is expressed as the internal precision, as each Ca subcut was only measured once. [b] The analytical uncertainty of the results is expressed as the external precision of two standard deviations (2SD). Each sample was measured ≥4 times. [c] $\delta^{44/40}$Ca of the first 20% Ca subcut of BHVO-2 was not obtained, because the filament was broken during TIMS measurement.

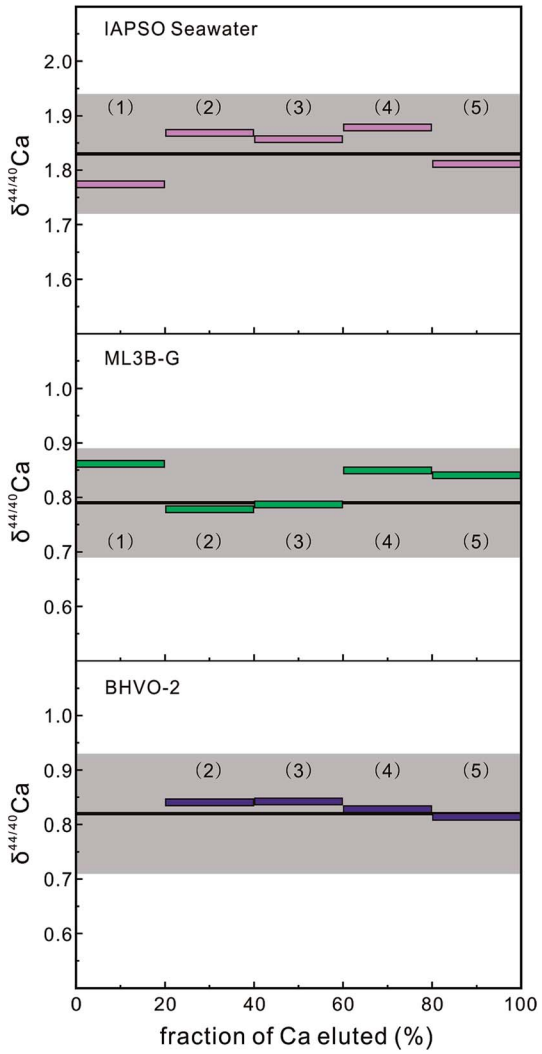

Fig. 2 $\delta^{44/40}$Ca of each Ca subcut of IAPSO seawater, ML3B-G and BHVO-2 after correction by the ^{42}Ca–^{43}Ca double spike technique with the exponential law. The solid black line and grey bar in each panel represent $\delta^{44/40}$Ca with full recovery. $\delta^{44/40}$Ca of the first Ca subcut of BHVO-2 was not obtained, because the filament was broken during TIMS determination.

that occurred during column separation[31] can be effectively corrected by the ^{42}Ca–^{43}Ca double spike using the exponential law. Poor recovery has a limited effect on $\delta^{44/40}$Ca when the Ca isotopes are determined using TIMS with the double spike technique.

4.2 Why does poor recovery have a limited effect on $\delta^{44/40}$Ca using the double spike technique?

The similar behavior of the Ca isotopes during column separation and TIMS determination can reasonably explain why Ca recovery is not a big issue for TIMS determination when the double spike technique is used. As for isotopic fractionation during column separation, Zhu *et al.*[31] investigated the behavior of Ca isotopes on a Bio-Rad AG MP-50 (100–200 mesh) resin column by measuring $\delta^{44/40}$Ca of IAPSO seawater in different Ca subcuts.[31] The slope of the measured $\ln(^{42}Ca/^{44}Ca)$ – $\ln(^{40}Ca/^{44}Ca)$ graph of all five Ca subcuts is 2.0483 (Fig. 3 in Zhu *et al.*[31]), which suggests that Ca isotopic fractionation occurring during column separation fits the exponential law well.[31]

Generally, the instrumental fractionation of Ca isotopes during TIMS determination also follows the exponential law.[20,47] However, in some cases, mixing reservoir effects on the filament could make the instrumental fractionation complex, such as by causing the raw data to deviate from the exponential law.[31,47,48] In our study, as shown in panels (1-a) to (5-a) in Fig. 3, the slope of the measured $\ln(^{42}Ca/^{44}Ca)_M - \ln(^{40}Ca/^{44}Ca)_M$ graph for each set of Ca subcut raw data for IAPSO seawater is close to 2.0483, which is similar to that of the exponential law (for more detailed information, see Zhu *et al.*[31]). Moreover, the measured isotope ratios ($\ln(^{40}Ca/^{42}Ca)_M$) nearly show a linear correlation with time (panels (1-b) to (5-b) in Fig. 3). These observations indicate that the mixing reservoir effects during TIMS determination were insignificant, so that the instrumental fractionation did not deviate from the exponential law.[31,48] Otherwise, the slope of the measured $\ln(^{42}Ca/^{44}Ca)_M - \ln(^{40}Ca/^{44}Ca)_M$ graph would deviate from the exponential law of 2.0483 and the measured isotope ratios would not show a linear correlation with time.[31,48]

Furthermore, for each Ca subcut, the degree of isotopic fractionation during analysis (defined as FD (‰), see the caption of Fig. 3 for the equation) is lower than the largest fractionation degree allowed within 0.1‰ precision of $\delta^{44/40}$Ca (termed FD_{max}; for more detailed information, see Zhu *et al.*[31]) (Fig. 4). In particular, different from the column separation with full recovery, this isotopic fractionation we observed for each Ca subcut with 20% recovery includes not only the instrumental fractionation, but also the isotopic fractionation that occurred

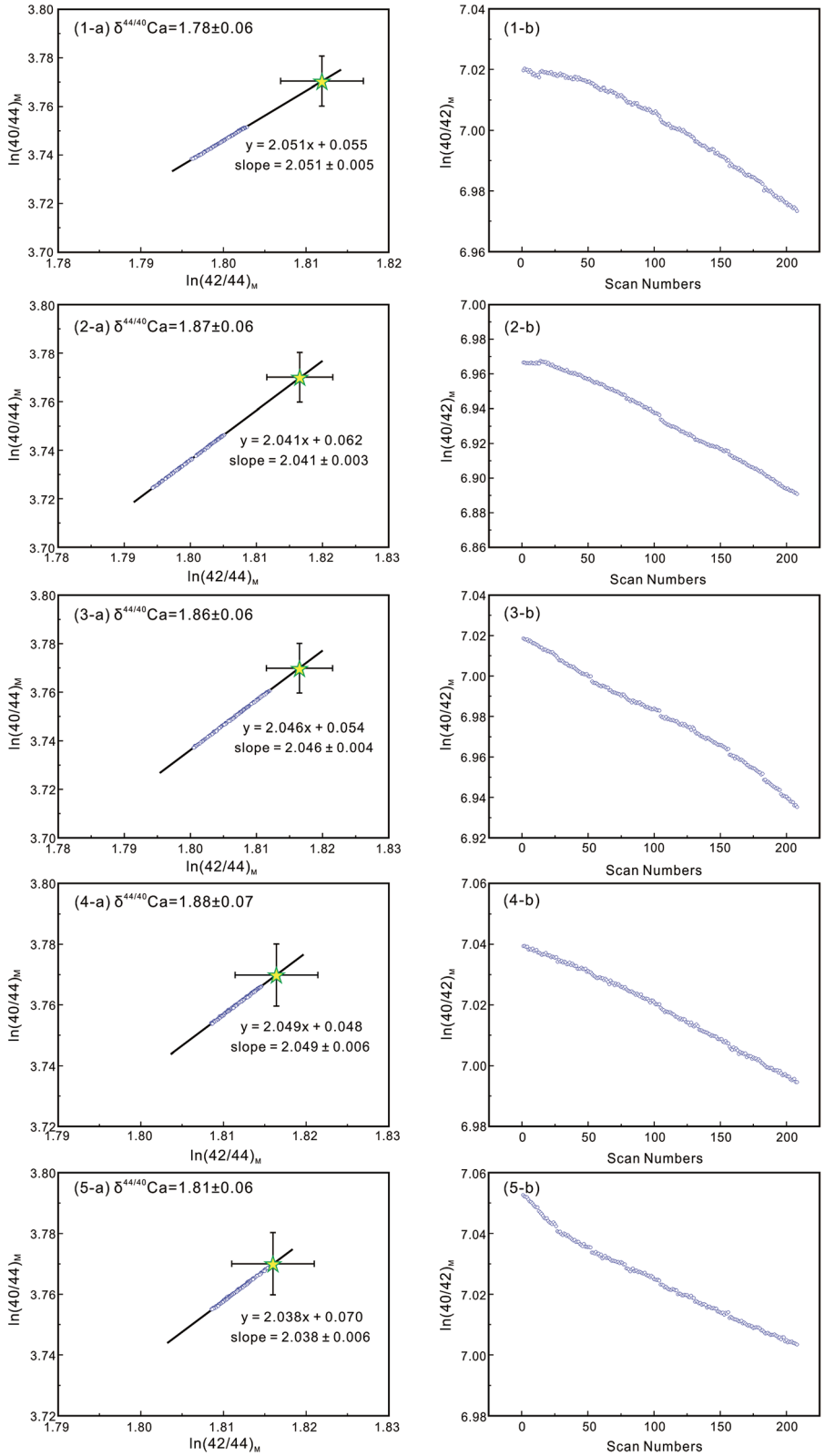

Fig. 3 $\ln(^{42}Ca/^{44}Ca)_M$ *vs.* $\ln(^{40}Ca/^{44}Ca)_M$ and $\ln(^{42}Ca/^{44}Ca)_M$ *vs.* scan numbers for TIMS runs of the five Ca subcuts of IAPSO seawater. Raw data (circles) and the calibrated average values after correction by the double spike technique (stars) are used to check the behavior and the degree of isotopic fractionation during analysis. The degree of isotopic fractionation during analysis can be calculated using the equation FD = $[(^{42}Ca/^{44}Ca)_M/(^{42}Ca/^{44}Ca)_C - 1] \times 1000$, where $(^{42}Ca/^{44}Ca)_C$ refers to the calibrated average values. The range bars in the panels (1-a) to (5-a) represent a fractionation degree of 5‰ from the calibrated average value.

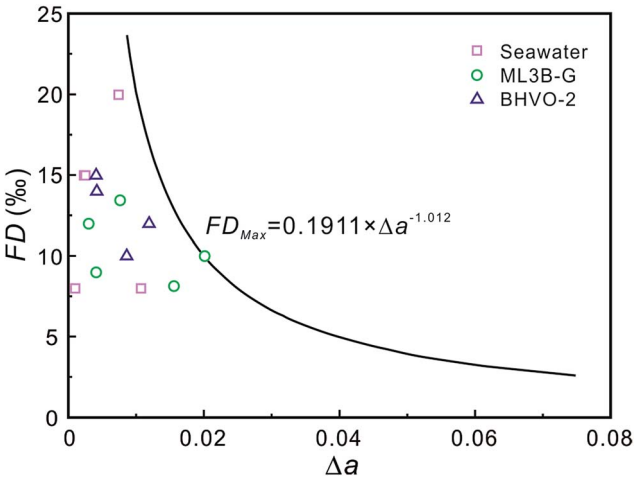

Fig. 4 The degrees of isotopic fractionation (FD (‰)) during the analysis of each subcut for IAPSO seawater, ML3B-G and BHVO-2 are lower than the largest fractionation degree allowed within 0.1‰ precision of $\delta^{44/40}$Ca (defined as FD_{max}).[31] The black curve represents the negative correlation between Δa and FD_{max} ($FD_{max} = 0.1911 \times \Delta a^{-1.012}$), where Δa in the formula represents the difference between the actual instrumental fractionation and the exponential law.[31]

during column separation. The instrumental fractionation degrees during TIMS determination are therefore definitely lower than FD_{max}, which further excludes the large uncertainties that may be caused by mixing reservoir effects.[31] Therefore, the double spike technique using the exponential law can exactly correct both the Ca isotopic fractionation that occurred during column separation and TIMS determination simultaneously, as proposed by previous studies.[20,23,49,50]

4.3 "Calcium peak cut" of column separation

In previous studies, to obtain a pure Ca cut, sample solutions with low CaO contents (*e.g.* orthopyroxene, olivine, peridotite and dunite) were usually passed through the column twice.[11,12] This method is time-consuming and costly. Our study suggests that the Ca recovery would be generously decreased to 20% when the matrix effects are complicated, and accurate Ca isotope data can still be obtained after correction using the double spike technique with the exponential law. Thus, a new "peak cut" procedure of column separation is proposed here for samples with low CaO contents, which means that we can pass through the column once and only collect the middle of the Ca eluate, abandoning both sides of the Ca eluate that overlap with other possible elements (*e.g.* K and Sr) to eliminate matrix effects (Fig. 5). It is noteworthy that the double spike must be added and mixed well with the samples before column separation, so that the Ca isotopic fractionation occurring during this process can be exactly corrected, along with instrumental mass bias correction, by the double spike technique.

The "Ca peak cut" procedure can be applied to other isotope systems as well, but two conditions should be satisfied: (1) the double spike needs to be properly mixed with the sample before column separation, and (2) the isotopic fractionation that occurs during column separation and TIMS determination

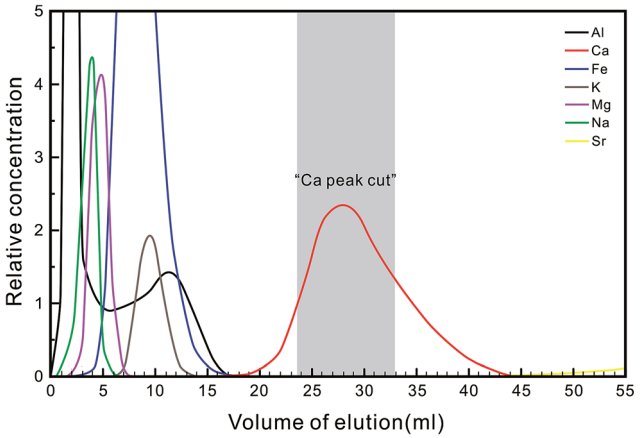

Fig. 5 The "peak cut" procedure of column separation for Ca isotope measurement using the double spike technique and TIMS.

must follow the same fractionation law. Otherwise, the isotopic fractionation that occurs during these two processes cannot be corrected properly by the double spike with the same fractionation law simultaneously. Large errors would be produced by correction with an improper fractionation law.[20,31] In addition, the behavior of instrumental fractionation for TIMS is generally influenced by mixing reservoir effects during heterogeneous evaporation from a filament, which would deviate the apparent instrumental fractionation from the exponential law.[31,48] Similarly, for a isotope system, there is a possibility that the isotopic fractionation occurring during column separation and mass determination does not follow the same fractionation law. To make sure the "peak cut" procedure is suitable for other isotope systems, it is essential to firstly investigate the detailed behavior of the isotopes during column separation and mass determination.

5 Conclusion

We measured $\delta^{44/40}$Ca of five purified Ca subcuts (*e.g.* 0–20, 20–40, 40–60, 60–80 and 80–100%) with recovery yields of about 20% for reference materials of IAPSO seawater, ML3B-G and BHVO-2 using TIMS. After correction using the ^{42}Ca–^{43}Ca double spike technique with the exponential law, $\delta^{44/40}$Ca of all Ca subcuts exhibit limited variation and are in great agreement with $\delta^{44/40}$Ca of the Ca cut with full recovery, within a margin of error. Our results demonstrate that both the Ca isotopic fractionation that occurred during column separation and TIMS determination can be corrected by the ^{42}Ca–^{43}Ca double spike technique with the exponential law. Therefore, our practices provide a "peak cut" procedure of column separation using the double spike technique, which can only collect the peak of a Ca cut after mixing the double spike with the sample solution. This procedure would significantly reduce matrix effects, especially for samples with low CaO contents. It is worth noting that during TIMS determination, mixing reservoir effects on the filament should be monitored to make sure that the apparent instrumental fractionation does not deviate from the

exponential law significantly. This "peak cut" procedure of column separation could be applied to other isotope systems if isotopic fractionation occurring during column separation and mass determination follow the same fractionation law.

Conflicts of interest

There are no conflicts to declare.

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References

1 D. J. DePaolo, *Rev. Mineral. Geochem.*, 2004, **55**, 255–288.
2 M. S. Fantle and E. T. Tipper, *Earth-Sci. Rev.*, 2014, **129**, 148–177.
3 A. Heuser and A. Eisenhauer, *Bone*, 2010, **46**, 889–896.
4 J. I. Simon, D. J. DePaolo and F. Moynier, *Astrophys. J.*, 2009, **702**, 707–715.
5 J. I. Simon and D. J. DePaolo, *Earth Planet. Sci. Lett.*, 2010, **289**, 457–466.
6 M. C. Valdes, M. Moreira, J. Foriel and F. Moynier, *Earth Planet. Sci. Lett.*, 2014, **394**, 135–145.
7 S. C. Huang and S. B. Jacobsen, *Geochim. Cosmochim. Acta*, 2017, **201**, 364–376.
8 J. I. Simon, M. K. Jordan, M. J. Tappa, E. A. Schauble, I. E. Kohl and E. D. Young, *Earth Planet. Sci. Lett.*, 2017, **472**, 277–288.
9 S. Huang, J. Farkaš and S. B. Jacobsen, *Geochim. Cosmochim. Acta*, 2011, **75**, 4987–4997.
10 F. Liu, X. Li, G. Wang, Y. Liu, H. Zhu, J. Kang, F. Huang, W. Sun, X. Xia and Z. Zhang, *J. Geophys. Res.: Solid Earth*, 2017, **122**, 9729–9744.
11 J.-T. Kang, H.-L. Zhu, Y.-F. Liu, F. Liu, F. Wu, Y.-T. Hao, X.-C. Zhi, Z.-F. Zhang and F. Huang, *Geochim. Cosmochim. Acta*, 2016, **174**, 335–344.
12 X. Zhao, Z. Zhang, S. Huang, Y. Liu, X. Li and H. Zhang, *Geochim. Cosmochim. Acta*, 2017, **208**, 368–380.
13 J.-T. Kang, D. A. Ionov, F. Liu, C.-L. Zhang, A. V. Golovin, L.-P. Qin, Z.-F. Zhang and F. Huang, *Earth Planet. Sci. Lett.*, 2017, **474**, 128–137.
14 H. Zhu, F. Liu, X. Li, G. Wang, Z. Zhang and W. Sun, *J. Geophys. Res.: Solid Earth*, 2018, DOI: 10.1002/2017jb014699.
15 J. Farkaš, F. Böhm, K. Wallmann, J. Blenkinsop, A. Eisenhauer, R. van Geldern, A. Munnecke, S. Voigt and J. Veizer, *Geochim. Cosmochim. Acta*, 2007, **71**, 5117–5134.
16 J. Farkaš, D. Buhl, J. Blenkinsop and J. Veizer, *Earth Planet. Sci. Lett.*, 2007, **253**, 96–111.
17 W. Stahl and I. Wendt, *Earth Planet. Sci. Lett.*, 1968, **5**, 184–186.
18 K. Heumann and W. Luecke, *Earth Planet. Sci. Lett.*, 1973, **20**, 341–346.
19 R. P. Meshcheryakov and Y. M. Stolbov, *Geochem. Int.*, 1967, **4**, 1001–1003.
20 W. A. Russell, D. A. Papanastassiou and T. A. Tombrello, *Geochim. Cosmochim. Acta*, 1978, **42**, 1075–1090.
21 A. Heuser, A. Eisenhauer, N. Gussone, B. Bock, B. T. Hansen and T. F. Nagler, *Int. J. Mass Spectrom.*, 2002, **220**, 385–397.
22 D. Hippler, A. D. Schmitt, N. Gussone, A. Heuser, P. Stille, A. Eisenhauer and T. F. Nagler, *Geostand. Newsl.*, 2003, **27**, 13–19.
23 M. Amini, A. Eisenhauer, F. Böhm, C. Holmden, K. Kreissig, F. Hauff and K. P. Jochum, *Geostand. Geoanal. Res.*, 2009, **33**, 231–247.
24 C. Holmden and N. Belanger, *Geochim. Cosmochim. Acta*, 2010, **74**, 995–1015.
25 S. C. Huang, J. Farkas and S. B. Jacobsen, *Earth Planet. Sci. Lett.*, 2010, **292**, 337–344.
26 M. E. Wieser, D. Buhl, C. Bouman and J. Schwieters, *J. Anal. At. Spectrom.*, 2004, **19**, 844–851.
27 M. Schiller, C. Paton and M. Bizzarro, *J. Anal. At. Spectrom.*, 2012, **27**, 38–49.
28 T. Tacail, P. Telouk and V. Balter, *J. Anal. At. Spectrom.*, 2016, **31**, 152–162.
29 S. Mondal and R. Chakrabarti, *J. Anal. At. Spectrom.*, 2018, **33**, 141–150.
30 W. Russell and D. Papanastassiou, *Anal. Chem.*, 1978, **50**, 1151–1154.
31 H. L. Zhu, Z. F. Zhang, G. Q. Wang, Y. F. Liu, F. Liu, X. Li and W. D. Sun, *Geostand. Geoanal. Res.*, 2016, **40**, 185–194.
32 J. Fietzke, A. Eisenhauer, N. Gussone, B. Bock, V. Liebetrau, T. F. Nägler, H. Spero, J. Bijma and C. Dullo, *Chem. Geol.*, 2004, **206**, 11–20.
33 B. Cenki-Tok, F. Chabaux, D. Lemarchand, A. D. Schmitt, M. C. Pierret, D. Viville, M. L. Bagard and P. Stille, *Geochim. Cosmochim. Acta*, 2009, **73**, 2215–2228.
34 F. Liu, H. L. Zhu, X. Li, G. Q. Wang and Z. F. Zhang, *Geostand. Geoanal. Res.*, 2017, **41**, 675–688.
35 F. Liu, H. L. Zhu, D. C. Tan, Y. F. Liu, J. T. Kang, J. M. Zhu, G. Q. Wang and Z. F. Zhang, *J. Chin. Mass Spectrom. Soc.*, 2016, **37**, 310–318.
36 Z. Zhang, H. Zhu, Y. Liu, J. Zhu, J. Kang, D. Tan, F. Liu and G. Wang, *AGU Fall Meeting Abstracts*, 2013, p. 2626.
37 Y. F. Liu, H. L. Zhu, F. Liu, G. Q. Wang, J. F. Xu and Z. F. Zhang, *Geochemical*, 2015, **44**, 469–476.
38 C. Holmden, *Saskatchewan Geological Survey*, 2005, vol. 1.
39 K. P. Jochum, B. Stoll, K. Herwig, M. Willbold, A. W. Hofmann, M. Amini, S. Aarburg, W. Abouchami, E. Hellebrand and B. Mocek, *Geochem., Geophys., Geosyst.*, 2006, **7**, 217–222.
40 L. P. Feng, L. Zhou, L. Yang, D. J. DePaolo, S. Y. Tong, Y. S. Liu, T. L. Owen and S. Gao, *Geostand. Geoanal. Res.*, 2017, **41**, 93–106.
41 Y. S. He, Y. Wang, C. W. Zhu, S. C. Huang and S. G. Li, *Geostand. Geoanal. Res.*, 2017, **41**, 283–302.

42 A. D. Anbar, J. E. Roe, J. Barling and K. H. Nealson, *Science*, 2000, **288**, 126–128.
43 T. Ohno and T. Hirata, *Anal. Sci.*, 2007, **23**, 1275–1280.
44 F. Z. Teng, M. Wadhwa and R. T. Helz, *Earth Planet. Sci. Lett.*, 2007, **261**, 84–92.
45 F. Huang, J. Glessner, A. Ianno, C. Lundstrom and Z. F. Zhang, *Chem. Geol.*, 2009, **268**, 15–23.
46 S. Wakaki and T. Tanaka, *Int. J. Mass Spectrom.*, 2012, **323–324**, 45–54.
47 S. R. Hart and A. Zindler, *Int. J. Mass Spectrom. Ion Processes*, 1989, **89**, 287–301.
48 M. S. Fantle and T. D. Bullen, *Chem. Geol.*, 2009, **258**, 50–64.
49 O. Eugster, F. Tera and G. Wasserburg, *J. Geophys. Res.*, 1969, **74**, 3897–3908.
50 K. Heumann and K. Lieser, *Zeitschrift für Naturforschung*, 1972, **27**, 126–133.