Measurement of $\delta^{44}\text{Ca}$ Using a $^{43}\text{Ca}-^{42}\text{Ca}$ Double-spike TIMS Technique

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Abstract

A new high precision, low mass-range, simultaneous multi-collection technique was developed for $\delta^{44}\text{Ca}$ measurements by thermal ionization mass spectrometry using a $^{43-42}\text{Ca}$ calcium double spike to correct for instrument mass discrimination. Previous attempts to measure Ca-isotopes by simultaneous multi-collection have failed to produce the improvements in precision predictable by ion counting statistics. We demonstrate, however, that by measuring four Ca ion beams ($^{40}\text{Ca}$, $^{42}\text{Ca}$, $^{43}\text{Ca}$, and $^{44}\text{Ca}$) in three collectors (Axial, L1, and H1), we reduce the relative mass separation in our isotope measurements from ~10% to 5%, which reduces imprecision generated by ion optical effects in the mass spectrometer. The external reproducibility of $\delta^{44}\text{Ca}$ values using this low mass-range technique is ±0.1‰ at the 95% confidence level, among the best precisions yet reported. Although tests are underway to further improve precision, the precision currently achievable is sufficient for $\delta^{44}\text{Ca}$ studies of carbonate diagenesis, dolomitization, and reservoir quality, as the expected $\delta^{44}\text{Ca}$ variation in carbonate minerals is ~3‰.

Keywords: Ca isotopes, double spike, petroleum research, isotope fractionation.

1. Introduction

A major thrust in petroleum research is to understand how diagenetic reactions in carbonate sediments and rocks contribute to porosity preservation and reservoir quality. Basic petrographic examination of rock mineralogy and texture, and elemental and isotopic geochemistry are used to unravel the diagenetic history of the reservoir, which in turn provides constraints on the sources of diagenetic fluids that have influenced the development of the reservoir, including petroleum migration.

Oxygen, carbon, and strontium isotopes have become indispensable tools in diagenesis research, but the tracer potential of the calcium isotopes, which make up 20 to 40 weight percent of carbonate rocks, has not been fully explored. One of the reasons for this is that the range of Ca isotope fractionation in Earth materials is relatively small (~1‰/amu), compared to O (~30‰/amu), and C isotopes (~60‰/amu). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary by 10‰ in diagenetic carbonates. The small range of Ca isotope variation requires high precision measurements that rely on either thermal ionization mass spectrometry (TIMS), or novel plasma ionization mass spectrometry (PIMS).

In this paper, the development of a multi-collector TIMS technique is reported for precise Ca isotope measurements using a $^{43}\text{Ca}-^{42}\text{Ca}$ double spike for correction of instrumental mass discrimination. External precision of $\delta^{44}\text{Ca}$ is ±0.1‰ at the 95% confidence level (n=18), which is among the best yet reported.

2. Requirements for Precise Measurement of Ca Isotopes

a) Counting Statistics

Counting statistics dictate that the lower abundance isotopes have higher measurement uncertainties. Calcium has one abundant isotope ($^{40}\text{Ca}$) and five minor isotopes ($^{42}\text{Ca}$, $^{43}\text{Ca}$, $^{44}\text{Ca}$, $^{46}\text{Ca}$, and $^{48}\text{Ca}$) (Table 1), making high precision measurements difficult to achieve. Precision may be improved by counting more atoms during a measurement session, either by generating higher intensity ion beams, or integrating lower intensity ion beams for longer periods of time during each scan of the mass spectrum. Some practical considerations, however, limit the intensity of Ca ion beams, the choice of integration time and, therefore, measurement precision. For example, TIMS instruments typically employ $10^{11}$ Ohm resistors in the Faraday cup amplifier circuits. The voltage differences that

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are measured across the resistors are proportional to the ion beam intensities. Unfortunately, the response is linear over a limited range of ion beam intensities. Therefore, ion beam intensities of the minor isotopes are limited by the maximum intensity of the major isotope, which for the $10^8$ Ohm resistor keeps $^{40}$Ca ion beams to $8 \times 10^{11}$ A, or lower. The intensities of the corresponding minor isotopes of Ca are between 40 and 800 times smaller. The Thermo-Finnigan Triton instrument used in this study employs $10^5$ Ohm resistors with a 50 V dynamic range, which means that the major ion beam can be four times larger than in mass spectrometers with conventional resistors. However, accelerated damage to the Faraday cups is a major complication of repeatedly making measurements at high ion beam intensities, which changes cup efficiency and the ‘absolute’ isotope ratios measured by simultaneous multi-collection.

### b) Single-Collector Peak Hopping vs. Simultaneous Multi-Collection

Calcium isotopes may be measured using a single Faraday collector by cycling the magnet field such that individual ion beams are collected at different times (single-collector peak hopping). The isotope ratios are then corrected for intensity changes during the measurement cycle caused by beam growth or decay (time-interpolation). If ion beam intensities are not stable (i.e., flat, or smoothly rising or falling), the time-interpolated, measured Ca isotope ratios will be subjected to a large uncertainty. Thus, integration times are normally of short duration (1 to 3 s) in order to limit the detrimental effects of irregular beam growth and decay, but this also limits the theoretically attainable precision of the measurements.

Modern mass spectrometers may have upwards of nine Faraday collectors for simultaneous collection of multiple ion beams. Because beam growth and decay affects all of the isotopes equally during multi-collector scans, integration times can be substantially lengthened, thus improving the precision of the measurements compared to single-collector peak hopping. One complication is that differences in amplifier gains between collectors must be precisely calibrated, which is performed by computer-controlled switching of a constant current into each Faraday cup amplifier circuit before the beginning of a measurement session. Another complication is that damage to individual Faraday collectors over time may change the measured isotope ratios. Two features of the Thermo-Finnigan Triton instrument used in this study that at least partially addresses these problems. Firstly, the amplifier circuits are effectively ‘rotated’ between all of the collectors, thus eliminating subtle differences in amplifier gains. Secondly, the Faraday collectors are machined from solid graphite, which slows the cumulative effects of ion beam damage.

### c) Ion Optical Effects

Because Ca has a wide mass spectrum, the full complement of the Ca isotopes (18% spread in relative atomic mass) exceeds the capacity of modern TIMS instruments to collect all six isotopes simultaneously. One solution to this problem is to make the measurements in two sets or ‘hops’ of the magnet position. The first hop measures masses 40 to 44 simultaneously, and the second hop measures masses 44 to 48. The Thermo-Finnigan Triton instrument used in this study features a mass dispersion of 15%, but the ~10% relative mass separation of just four of the calcium isotopes still places the off-axis Ca ion beams close to the inner walls of the spectrometer flight tube where they may be clipped by baffles or where positive ions may be neutralized by free electrons. Thus, for elements like Ca with a wide mass spectrum, the collection efficiency may be proportional to the ion optical path through the spectrometer.

The ion optical effects in the mass spectrometer that result from the wide mass range of the Ca isotopes are widely considered to be the major practical impediment to achieving the external precisions predicted by ion counting statistics for multi-collection strategies (Fletcher et al., 1997; DePaolo, 2004). For example, DePaolo (2004) reported excellent internal precision (≈0.05%) for Ca isotope measurements using a multi-collection technique on a VG 354 instrument, but poor inter-sample reproducibility (external precision, ±0.5%, 2σ). This was attributed to subtle differences in focusing from sample to sample, exacerbated by ion optical effects. Fletcher et al. (1997) also reported difficulties with static multi-collection measurements on a VG 354 instrument. Heuser et al. (2002) published a multi-collection routine for Ca isotope measurements on a Finnigan-MAT 262 instrument, but failed to achieve any increase in external precision over single-collector peak hopping on the same instrument (±0.25%, 2σ). Although the reasons for this were not discussed in Heuser et al. (2002), in keeping with the observations of Skulan et al. (1997) and Fletcher et al. (1997), it is likely that ion optical effects were responsible.

### Table 1 - Atom percent isotope abundances in CaF$_2$ standard and 43-42 double spike.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{40}$Ca</th>
<th>$^{42}$Ca</th>
<th>$^{43}$Ca</th>
<th>$^{44}$Ca</th>
<th>$^{46}$Ca*</th>
<th>$^{48}$Ca*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$ standard</td>
<td>96.98233</td>
<td>0.642097</td>
<td>0.133424</td>
<td>2.05676</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Double spike</td>
<td>6.07891</td>
<td>77.93838</td>
<td>14.41666</td>
<td>1.54069</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>* not measured</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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d) Double Spiking

When stable isotope measurements are performed on a TIMS instrument, double spiking may be used to correct the instrumental mass discrimination for elements with four or more isotopes. The ‘spike’ consists of a solution made from material that has been artificially enriched in one of the isotopes. A double spike is prepared by mixing two spike solutions (each with a different enriched isotope) in the desired proportion. Isotopically enriched material may be purchased from a number of sources like the Oak Ridge National Laboratory in the U.S. The isotope ratios in the double spike may be determined by analysis of spike/standard mixtures. This approach assumes that the isotope ratios of the standard are known to within a mass fractionation factor of their true values. Knowing the isotope ratios of the standard, the double-spike isotopes are subtracted from the mixed composition runs using an iterative spike-unmixing routine written in Excel. This procedure yields a precise isotope analysis of the double-spike ratio relative to the isotope ratio in the standard. Uncertainty in the double-spike composition does not factor significantly into the uncertainty of the Ca isotope determinations because δ²⁴⁴Ca values reflect isotope ratio differences between samples and standards.

Practically every conceivable double-spike combination has been used to correct TIMS measurements of Ca isotopes for instrumental discrimination. Russell et al. (1978) adopted a 48-42 double-spike, and a single-collector peak hopping technique. A similar strategy was followed by Skulan et al. (1997), Zhu and McDougall (1998), and Lemarchand et al. (2004). Multi-collector techniques were presented by Heuer et al. (2002) using 43-48 double spike, and Fletcher et al. (1997) using a 43-46 double spike.

e) Mass Spectrometry and Choice of Ca Double Spike

Recognizing that focusing and ion optical issues have hampered precise Ca isotope measurements (Fletcher et al., 1997; Skulan et al., 1997; DePaolo, 2004), a 43-42 double spike was chosen in order to reduce the relative mass separation of the multi-collector measurements. Four isotopes of Ca are measured (⁴⁰Ca, ⁴２Ca, ⁴３Ca, and ⁴⁴Ca) in two ‘hops’ of the magnetic field. The first hop places ⁴⁰Ca in the axial collector, which is the optimal position from the perspective of ion optical aberrations, ⁴３Ca in the L1 collector, and ⁴２Ca in the H1 collector (Figure 1). The magnet is then switched, putting ⁴⁰Ca in the L1 collector and ⁴２Ca in the H1 collector. This dynamic routine allows three isotope ratios to be determined: 43/42, 44/42 from the first hop, and 40/42 from the second hop. The measurements from the two hops are related through the 40/44 ratio. This dynamic, multi-collection strategy reduces the relative mass separation from ~10% to ~5%. But the results of the measurements performed at high relative mass separation, with ⁴⁰Ca collected in the L3 position, are also reported for comparison.

The double spike was calibrated against a Saskatchewan Isotope Lab gravimetric CaF₂ standard (SIL)-CaF₂) with a ‘normal’ isotope composition. The abundances of selected Ca isotopes in this standard were measured on a Thermo-Finnigan Triton instrument using the low relative mass separation measurement routine and are reported in Table 1. Internal isotope normalization of the standard was performed using a ⁴⁰Ca/⁴⁴Ca ratio of 47.153. This is the value determined by Russell et al. (1978) using a gravimetrically determined ⁴⁰Ca/⁴⁴Ca double spike. Thus, the absolute ratios of our Ca determinations are tied to the Russell et al. (1978) values. Because different laboratories use different normalization and spike calibration procedures, the ‘absolute’ Ca isotopic ratios are variable between laboratories, but the isotope ratio differences (δ²⁴⁴Ca) are comparable. The calibrated 43-42 double-spike composition is given in Table 1 for selected Ca isotopes.

f) Method

Samples and standards were mixed with the 43-42 double spike prior to mass spectrometry, and prior to purification by cation exchange chromatography, in the case of natural samples. Natural samples of Ca must be purified to remove potassium because ⁴⁰K interferes on ⁴⁰Ca.

About 3 to 5 µg of Ca (in the nitrate form) are loaded onto the side filament of a double Re filament assembly. The ionization filament current is held at 3.0 A. The evaporation filament current is usually about 0.2 A at the start, and is raised during the run, under computer control, to maintain a stable ion beam intensity of about 8.0 x 10⁻¹³ A of ⁴⁰Ca. Samples were heated and focused manually, and after the start of the run, peak centering and focus checks were performed under computer control. Integration times were 16 s for each hop, with a 6 s measurement delay time between
hops to allow for the decay of the previous signals. Amplifiers were rotated to negate the effect of differences in amplifier gains. Defocused baselines were performed at the beginning of each block (18 times). A single Ca isotope measurement comprises 180 scans.

3. Results and Discussion

a) Reproducibility of the $^{40}\text{Ca}/^{44}\text{Ca}$ Ratio

The reproducibility of $^{40}\text{Ca}/^{44}\text{Ca}$ is based on 18 measurements of the SIL-CaF$_2$ standard performed over a period of four months (Table 2). On the whole, the external precision of the measurements performed at low relative mass separation ($\pm 0.1\%_{\text{SE}}$) is four times better over this period than the corresponding measurements performed at high relative mass separation ($\pm 0.45\%_{\text{SE}}$) at the 95% confidence level. A closer look at the individual measurements, however, reveals a shift in the $^{40}\text{Ca}/^{44}\text{Ca}$ ratios for the measurements performed at high relative mass separation in the week of February 22, 2005 (Figure 2). The timing of the shift corresponds with the removal of the original ion source, and replacement with a spare ion source. It is unclear how the spare ion source has caused the measurements performed at high relative mass separation to shift this dramatically, but the fact that the corresponding measurements performed at low relative mass separation were largely unaffected, suggests that: 1) focusing and ion optical effects are responsible, and 2) that the measurements performed at low relative mass separation are resistant to focusing and ion optical peculiarities. More time is needed before it will be known whether the offset is temporary due to some transient problem with focusing, or a permanent feature of the spare ion source.

Ignoring the shift in $^{40}\text{Ca}/^{44}\text{Ca}$ ratios, and instead focusing on the pre-shift and post-shift measurements, those performed at both low and high relative mass separation have nearly the same precision. But the latter give lower $^{40}\text{Ca}/^{44}\text{Ca}$ ratios by about 0.25‰ for the measurements made with the original ion source, and 0.7‰ for the spare ion source. The lower $^{40}\text{Ca}/^{44}\text{Ca}$ ratios for the measurements performed at high relative mass separation are consistent with the reduction in the $^{40}\text{Ca}$ ion beam intensity due to ion optical effects. The $^{40}\text{Ca}$ ion beam is furthest from the axial collector and, therefore, closest to the wall of the flight tube where the ion beam may be clipped by baffles, or partially neutralized by free electrons.

b) $^{40}\text{Ca}/^{44}\text{Ca}$ Ratio of Caribbean Seawater and Carbonates

$^{40}\text{Ca}/^{44}\text{Ca}$ ratios are reported for Caribbean seawater from Punta Maroma, MX (Table 2). Although it is difficult to compare ‘absolute’ Ca isotope ratios of samples between laboratories, one may compare $^{44}\text{Ca}$ values of Punta Maroma carbonates with other carbonates in the literature, by normalizing to seawater as a standard. Two carbonates, a calcareous algae and a coral, are -1.2‰ depleted of $^{44}\text{Ca}$ compared to contemporaneous seawater, in agreement with literature values, which show $^{44}\text{Ca}$ depletions ranging from -0.9 to -2.5‰.

c) Measured vs. Theoretical Precision

One advantage of double spiking is the increase in ion beam intensity of at least two low abundance isotopes, like masses 43 and 42 in the present example. Therefore, double spike measurements yield improved precisions over, for example, unspiked PIMS measurements because of the better counting statistics. The theoretical ‘internal’ precision of the double-spiked $^{40}\text{Ca}/^{44}\text{Ca}$ measurements is $\pm 0.02$ (2$\sigma$). The observed internal precision is 0.03‰, which is reasonably close to the theoretical limit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{40}\text{Ca}/^{44}\text{Ca}$</th>
<th>2$\sigma$ % (rsd)</th>
<th>$\delta^{44}\text{Ca}$ (% Seawater)</th>
<th>Number of Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$ standard</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low mass separation</td>
<td>47.152</td>
<td>0.10</td>
<td>-1.27</td>
<td>18</td>
</tr>
<tr>
<td>High mass separation</td>
<td>47.136</td>
<td>0.45</td>
<td>-0.93</td>
<td>18</td>
</tr>
<tr>
<td>Punta Maroma Lagoon, MX*</td>
<td>47.092</td>
<td>0.07</td>
<td>0.00</td>
<td>5</td>
</tr>
<tr>
<td>Punta Maroma carbonates*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halimeda Tuna</td>
<td>47.148</td>
<td>0.024</td>
<td>-1.19</td>
<td>1</td>
</tr>
<tr>
<td>Colpophylia natans</td>
<td>47.146</td>
<td>0.024</td>
<td>-1.15</td>
<td>1</td>
</tr>
</tbody>
</table>

* low mass separation results
Figure 2 - $^{40}$Ca/$^{44}$Ca ratios of the SIL-CaF$_2$ standard measured in a four-month period beginning in November 2004. The dates on the x-axis correspond to measurements made in that particular week. In the week of February 22, 2005, the ion source of the mass spectrometer was changed. This caused a shift of $\sim-0.7\%$ in the $^{40}$Ca/$^{44}$Ca ratios performed at high relative mass separation. The $^{40}$Ca/$^{44}$Ca ratios performed at low relative mass separation shifted by only $-0.07\%$ on average. The reason for the shift is not known, but the fact that measurements at low mass separation were relatively unaffected points to ion optics and focusing in the mass spectrometer as the likely problem. The original ion source (November to December) produced a much smaller offset of about $-0.25\%$ between $^{40}$Ca/$^{44}$Ca ratios measured at low and high relative mass separation.

Reproducibilities of $^{44}$Ca measurements reported from other laboratories are listed in Table 3. It is noted that a large range of precisions is achieved, ranging from 0.1 to 0.5\% (2σ). The external precision reported in this paper ($\pm0.1\%$) is among the best of the reported values, similar to the best precisions reported for single-collector peak hopping (Skulan et al., 1997; DePaolo, 2004; Lemarchand et al., 2004). Single-collector peak hopping has the advantage of being unaffected by ion optical effects because all of the isotopes are measured in a single collector and, thus, the ion beams follow the same optical path through the mass spectrometer. As stated earlier, however, very stable ion beams are needed over many hours to achieve this level of precision, and so it seems likely that for practical reasons 0.1\% is the optimal precision that may be achieved by single-collector peak hopping. Multi-collection measurements appear to offer the only way to further improve the precision of Ca isotope measurements, but at present ion optical/focusing effects need to be better controlled.

The external precision of multi-collector Ca isotope measurements reported in this paper using the Thermo-Finnigan Triton instrument is better than in laboratories using the VG 354 instrument (Skulan et al., 1997; De Paolo, 2004) or the Finnigan MAT 262 instrument (Hueser et al., 2002). The only other Triton measurements of Ca isotopes are those reported in Kasemann et al. (2005). These authors achieved $\pm0.1\%$ reproducibility of $^{44}$Ca at the 95\% confidence level using a 48-43 double spike. This choice of double spike indicates that their measurements were performed at high relative mass separation; however, the authors provide few details of their methodology, and no discussion of ion optical effects. It has been demonstrated in this study that multi-collector measurements performed at high relative mass separation are almost as precise as measurements made at low relative mass separation, in agreement with Kasemann et al. (2005), but offset in absolute value. It has also been shown that swapping the ion source produced a large shift in the measurements performed at high relative mass separation, but only a very small corresponding shift in the measurements made at low relative mass separation. This suggests that a 43-42 double spike and measurements made at low mass separation are effective at reducing ion optical aberrations, and may yield a more reliable, external precision of $^{44}$Ca over the longer term.
Table 3 - Comparison of external precisions in $^{44}\text{Ca}$ measurements between different labs.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>$\delta^{44}\text{Ca}$ ($\pm 2\sigma$)</th>
<th>$%$/amu ($\pm 2\sigma$)</th>
<th>Instrument</th>
<th>Measurement Technique*</th>
<th>Mass Discrimination Correction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saskatchewan Isotope Lab</td>
<td>0.1</td>
<td>0.025</td>
<td>TIMS, Triton</td>
<td>MC</td>
<td>43-42 double spike</td>
<td>this paper</td>
</tr>
<tr>
<td>Bristol</td>
<td>0.1</td>
<td>0.025</td>
<td>TIMS, Triton</td>
<td>MC</td>
<td>48-43 double spike</td>
<td>Kasemann et al. (2005)</td>
</tr>
<tr>
<td>Kiel</td>
<td>0.2</td>
<td>0.05</td>
<td>PIMS, Axiom</td>
<td>MC</td>
<td>standard bracketing</td>
<td>Fietzke et al. (2004)</td>
</tr>
<tr>
<td>Thermo-Finnigan</td>
<td>–</td>
<td>0.05</td>
<td>PIMS, Neptune</td>
<td>MC</td>
<td>standard bracketing</td>
<td>Wieser et al. (2004)</td>
</tr>
<tr>
<td>Caltech</td>
<td>0.12</td>
<td>0.03</td>
<td>TIMS, Lunatic</td>
<td>SC</td>
<td>48-42 double spike</td>
<td>Lemarchand et al. (2004)</td>
</tr>
<tr>
<td>Strasbourg</td>
<td>0.2</td>
<td>0.05</td>
<td>TIMS, VG</td>
<td>?</td>
<td>48-43 double spike</td>
<td>Schmitt et al. (2003)</td>
</tr>
<tr>
<td>GEOMAR</td>
<td>0.5</td>
<td>0.125</td>
<td>TIMS, 262</td>
<td>MC</td>
<td>48-43 double spike</td>
<td>Heuser et al. (2002)</td>
</tr>
<tr>
<td>Scripps</td>
<td>0.23</td>
<td>0.0575</td>
<td>TIMS, VG 54E</td>
<td>SC</td>
<td>48-42 double spike</td>
<td>Zhu and MacDougall (1998)</td>
</tr>
<tr>
<td>Oxford</td>
<td>–</td>
<td>0.05</td>
<td>PIMS, Nu</td>
<td>MC</td>
<td>standard bracketing</td>
<td>Halicz et al. (1999)</td>
</tr>
<tr>
<td>Curtain</td>
<td>0.4</td>
<td>0.1</td>
<td>TIMS, VG 354</td>
<td>MC</td>
<td>46-43 double spike</td>
<td>Fletcher et al. (1997)</td>
</tr>
<tr>
<td>Berkeley</td>
<td>0.1 to 0.2</td>
<td>~0.0375</td>
<td>TIMS, VG 354</td>
<td>SC</td>
<td>48-42 double spike</td>
<td>Skulan et al. (1997)</td>
</tr>
<tr>
<td>Caltech</td>
<td>0.5</td>
<td>0.125</td>
<td>TIMS, Lunatic</td>
<td>SC</td>
<td>48-42 double spike</td>
<td>Russell et al. (1978)</td>
</tr>
</tbody>
</table>

* MC, simultaneous multi-collection; SC, time-interpolated single collector peak hopping.

d) TIMS vs. PIMS Measurements of Ca Isotopes

How do the external precisions of TIMS and novel PIMS measurements compare? There are three papers published thus far on multi-collector plasma ionization mass spectrometry (PIMS) techniques for Ca isotope measurements (Halicz et al. 1999; Fietzke et al., 2004; Wieser et al. 2004). Even though the ion optical issues are less of a concern for the plasma ion source, the external precision is two times worse than for TIMS (Table 3). Ion optical effects are reduced in PIMS because samples are introduced into the plasma as a solution. In TIMS, ion beam focusing begins with the position of the solid Ca sample on the filament, which can change from sample to sample. Also, the filament must be properly aligned to the ion source steering plates, and to the ionization filament for double and triple filament assemblies. Therefore, each sample of Ca exhibits slightly different focusing characteristics that in a subtle way may contribute to the degradation of the reproducibility of $\delta^{44}\text{Ca}$. Additionally, the standard-bracketing technique commonly used in PIMS studies will mask the presence of ion optical effects because of normalization of the sample to the standard, in the same mass spectrometer run. In summary, therefore, the lower reproducibility of PIMS measurements must be due to factors other than ion optical effects like, for example, unresolved isobaric interferences, and slight (but significant) differences in chemical matrix between purified solutions of sample Ca, and the Ca-standard solutions to which the samples are compared. Matrix differences may cause slight differences in instrumental mass discrimination factors between samples and standard that are not eliminated by standard bracketing.

4. Conclusions

A low relative mass separation multi-collector technique for precise Ca isotope analysis using a 43-42 double spike has been developed. With this technique, and the latest generation TIMS mass spectrometer (Thermo-Finnigan Triton), it appears possible to largely overcome ion optical/focusing effects that hampered the development of simultaneous multi-collection strategies in the past. This is a significant breakthrough because increased precision is critical for development of a variety of Ca isotope proxy systems given the relatively small range of Ca isotope variation in nature. If ion optical/focusing effects can be further brought under control, it should be possible to achieve external precisions of less than 0.1‰ on $\delta^{44}\text{Ca}$. Although testing is being undertaken to further improve the external precision, it is good enough at present to begin pioneering $\delta^{44}\text{Ca}$ investigations of carbonate diagenesis, dolomitization, and reservoir quality.

5. Acknowledgments

Discussions with Dimitri Papanastassiou provided guidance and insight into the finer details of mass spectrometry during a sabbatical visit to Caltech/JPL in the spring of 2004. Thanks also to Bruce Eglington for managing the SIL, and Tim Propkopiuk for running day-to-day activities in the laboratory, thus, freeing the time needed to conduct this work. Dario Piotto is thanked for preparing perfectly orthogonal mass spectrometer filaments. Bill Patterson and Bruce Eglington are thanked for their comments on an earlier version of this manuscript.
6. References


