Application Note: 30018

Advances in High Precision Isotope Ratio Measurements of Calcium Using TI-MS

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Key Words

- TRITON
- Calcium
- High Dynamic Range
- Static Mode
- TI-MS

Introduction

Since the pioneering work of Russell et al. (1978), many geochemists have applied calcium isotope measurements to earth science problems. Calcium isotope measurements have proven useful in geochronologic studies (Marshall and DePaolo, 1982), especially when comparing the behavior of argon and calcium (Marshall et al., 1986). Variation in initial radiogenic calcium-40 can reveal the fractionation of potassium from calcium during igneous processes yielding useful information regarding the origin of ultrapotassic rocks and granites (Marshall and DePaolo, 1989).

More recently, the isotopic fractionation of calcium in the oceans has suggested application to paleoceanography (De La Rocha and DePaolo, 2000). In these studies, the precision of the calcium isotope ratios made by thermal ionization mass spectrometry (TI-MS) are on the order of 100 ppm (2σ); in most cases this limits the widespread application of calcium isotopes in geochemistry.

Calcium isotopes may also be measured on MC-ICP-MS (e.g. Halicz et al, 1999), but this technique is likely to be less accurate than TI-MS due to spectral interferences.

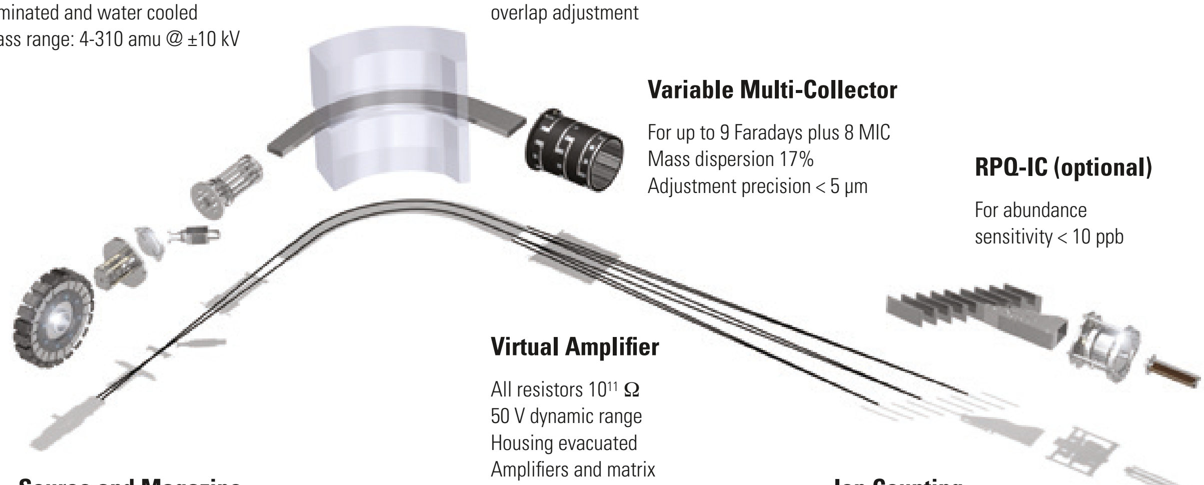
In our recent study, high precision calcium analyses were performed on the Thermo Scientific TRITON in Thermal Ionization mode (TI-MS).

Due to its increased dynamic range to 50 Volts @ 10^{11} Ω, novel ion collectors with unique solid graphite cups, excellent amplifier performance, and innovative new features, like the Virtual Amplifier and the Dynamic Zoom, the TRITON TI-MS ensures precise and accurate analyses.

Neodymium and strontium can be analyzed with guaranteed internal and external precisions better than 5 ppm (1σ).

Our studies on calcium especially benefit from these features and demonstrate improved internal and external precisions on **^{40}Ca/^{44}Ca of better than 25 ppm (1σ)**, approaching theoretical limits.

Experimental



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Sample and Analysis Parameter

Sample
$CaCO_3$ (Laboratory Standard) in 1% HNO_3
Concentration: 1 µg/µl

Amount
4 µg loaded (4 x 1µg)

Filaments
Double Filament Technique
Rhenium Ribbon (Cross "zone refined")
Filaments out-gassed prior to sample loading at 3.5 A

Loading
Sample solution heated to dryness at 0.5 A
60 sec. at 1.5 A, then 30 sec. at 2.0 A

MS-Condition

Accelerating Voltage:	10,000 Volt, positive
Ion source vacuum:	< 2 x 10^{-7} mbar
Analyzer vacuum:	< 2 x 10^{-9} mbar
Amplifier	Resistors: 10^{11} Ω, Stability: < 10 µV/h
Amplifier gains:	Gs < 10 ppm/day, Virtual Amplifier rotation

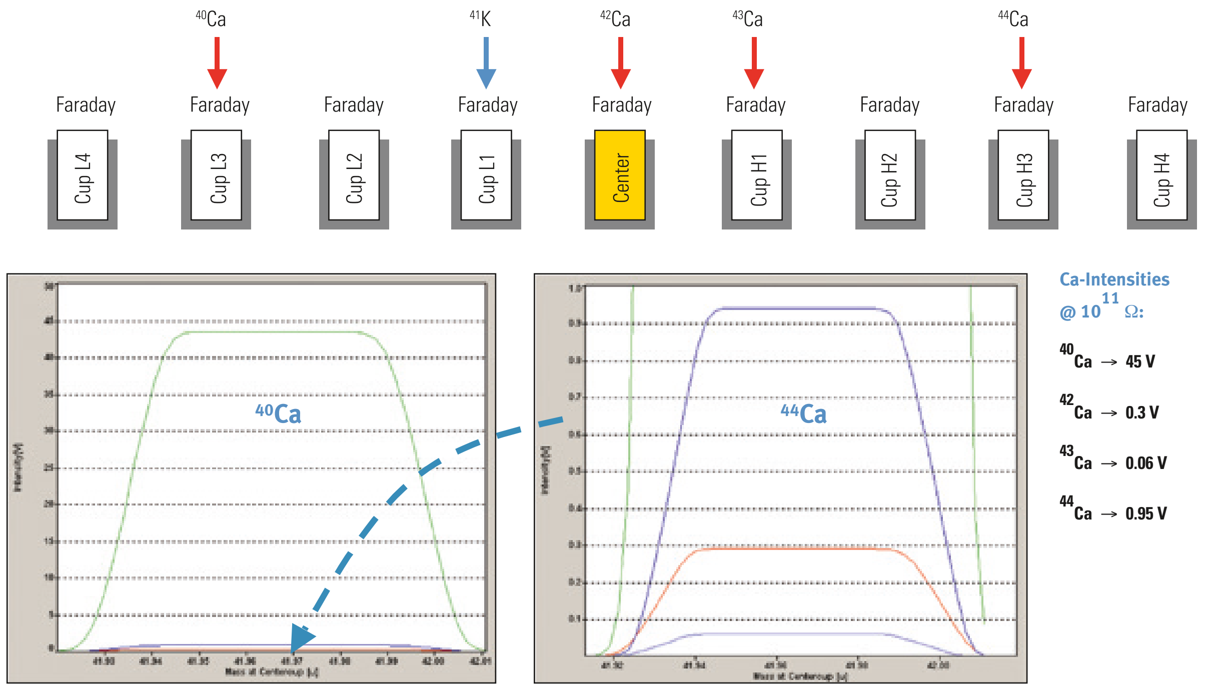
Sample Heating
Ionization Fil. to 2900-3100 mA within 10 minutes
Evaporation Fil. about 400 mA within 10 minutes
Target signal: 45 Volt @ ^{40}Ca

Data Collection
Measurements in static data collection mode
Typically 150 data per run
Integration time: 16 sec. for each data set (cycle)
Amplifier baselines: 67 sec. between data blocks of 10 cycles

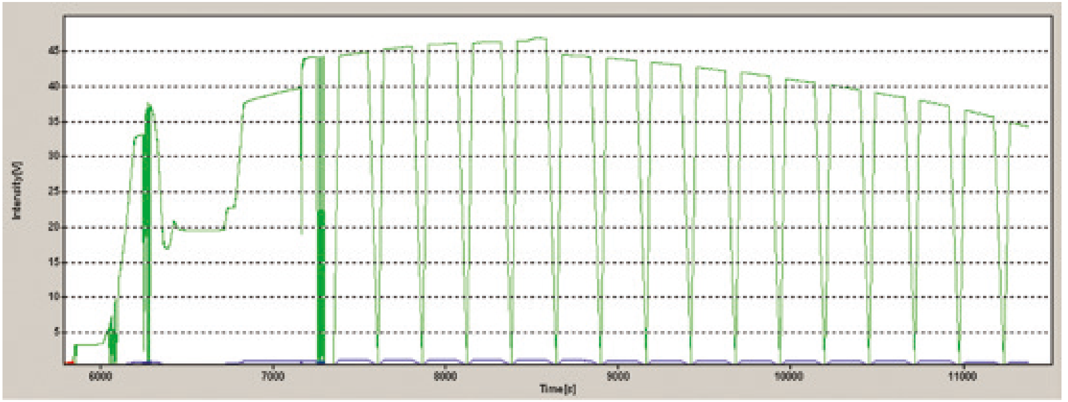
Evaluation
Fractionation correction using "Exponential Law"
Normalizing Ratio: $^{42}Ca/^{44}Ca = 0.31221$
Outlier test using 2σ-criterion
Interfering ^{40}K monitored, no correction needed

Thermo Scientific TRITON Thermal Ionization Mass Spectrometer

Setup of Faraday Cups for Ca Measurement



Emission Profile of a Typical Run

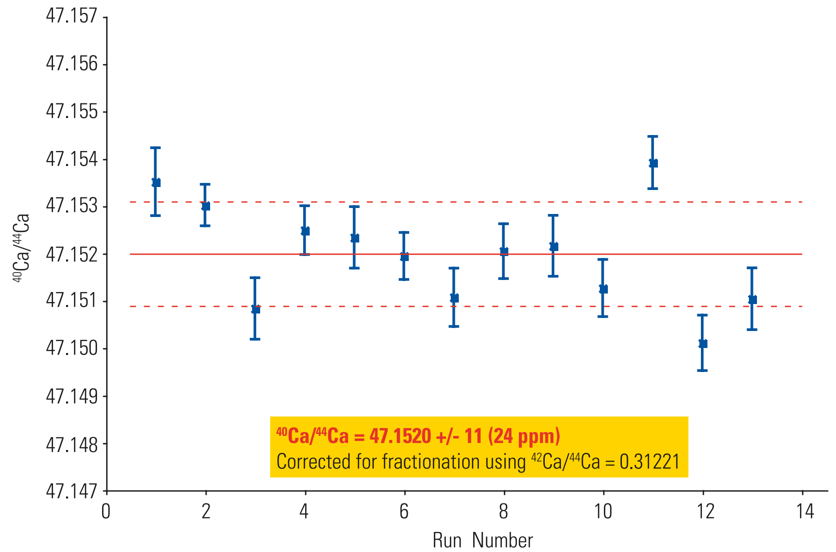


Results and Summary

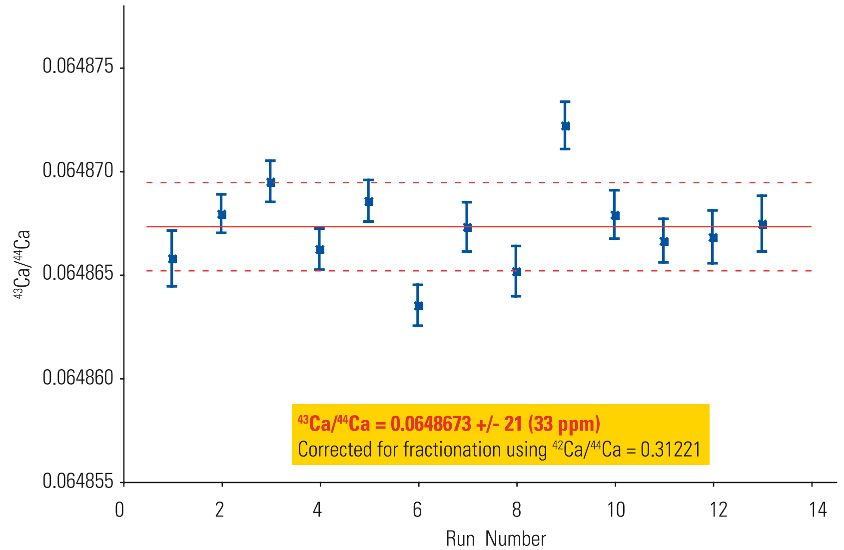
- The increased dynamic range of the TRITON TI-MS allows Ca-measurements at intensities up to 50 Volt without resistor change of current amplifiers. **Intensities for ^{40}Ca during analyses: 35 – 45 Volt.**
- Precision and reproducibility of analyses are significantly improved by:
  - Optimized low noise current amplifiers
  - Virtual Amplifier Concept to avoid cross calibration errors
- The flexible collector array allows analyses of the minor isotopes ^{46}Ca and ^{48}Ca together with ^{44}Ca in a 2nd step.
- In contrast to ICP-MS, TI-MS can be used to measure 40Ca directly with highest precision in static mode without any interference correction.
- Achieved precisions are

	External (1σ)	Internal ($1\sigma_E$) (average)
$^{40}Ca/^{44}Ca$	24 ppm	13 ppm
$^{43}Ca/^{44}Ca$	33 ppm	18 ppm

Fractionation corrected by "Exponential Law" using $^{42}Ca/^{44}Ca = 0.31221$



$^{40}Ca/^{44}Ca$ - External reproducibility



$^{43}Ca/^{44}Ca$ - External reproducibility

References

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