

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

Dietmar Tuttas, Johannes B. Schwieters, Thermo Fisher Scientific, Bremen, Germany

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 @ $10^{11} \Omega$, 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 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 $^{40}\text{Ca}/^{44}\text{Ca}$ of better than 25 ppm (1σ), approaching theoretical limits.

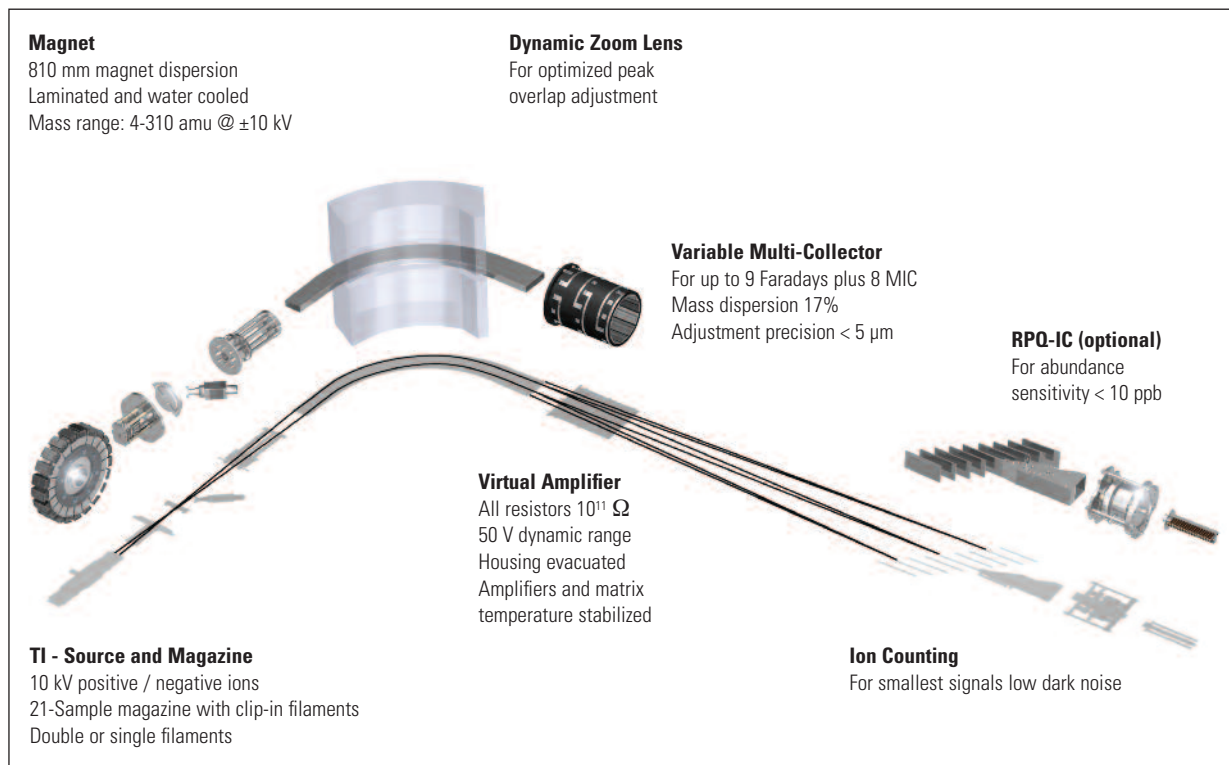


Thermo Scientific TRITON Thermal Ionization Mass Spectrometer

Key Words

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

Experimental



Sample and Analysis Parameter

Sample:

CaCO₃ (Laboratory Standard) in 1% HNO₃
Concentration: 1 μg/μl

Amount:

4 μg loaded (4 x 1 μg)

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: | 10000 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 @ ⁴⁰Ca

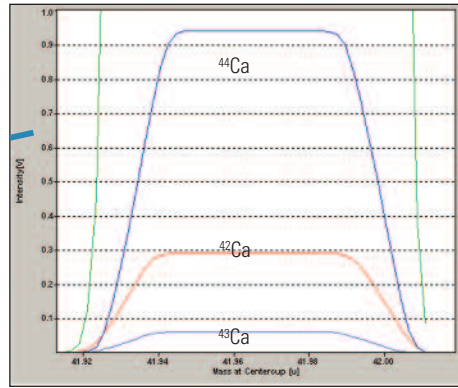
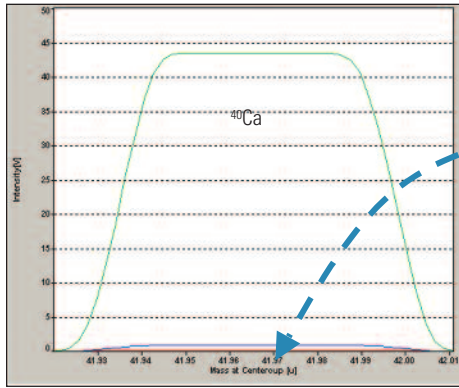
Data Collection:

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: ⁴²Ca/⁴⁴Ca = 0.31221
Outlier test using 2σ-criterion
Interfering ⁴⁰K monitored, no correction needed

Setup of Faraday Cups for Ca Measurement



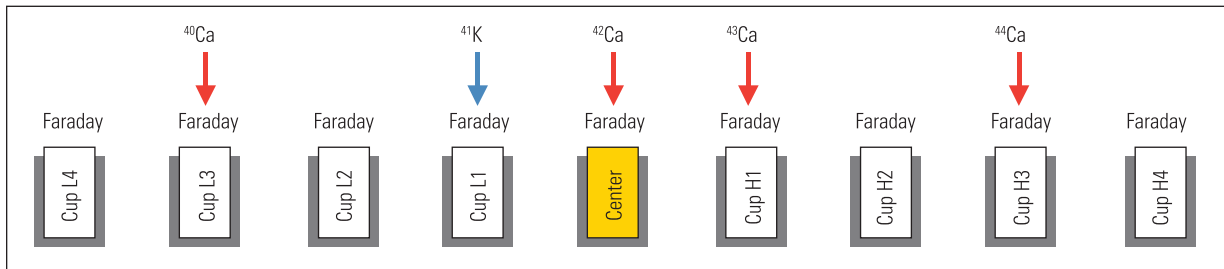
Ca-Intensities
@ $10^{11} \Omega$:

$^{40}\text{Ca} \rightarrow 45 \text{ V}$

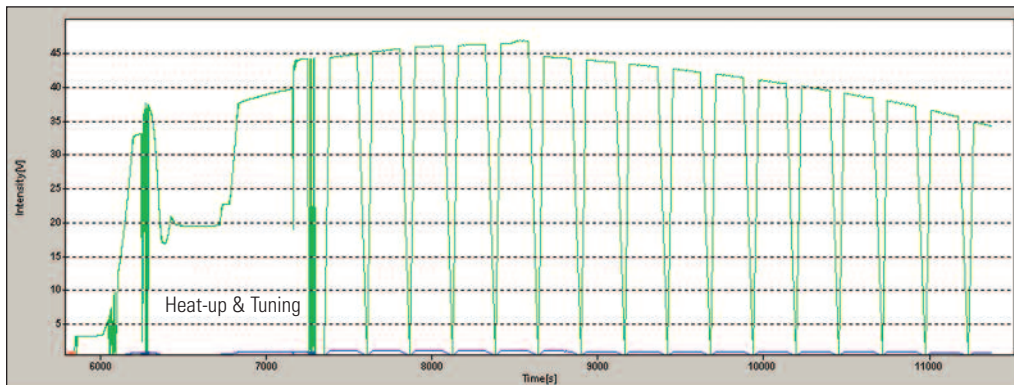
$^{42}\text{Ca} \rightarrow 0.3 \text{ V}$

$^{43}\text{Ca} \rightarrow 0.06 \text{ V}$

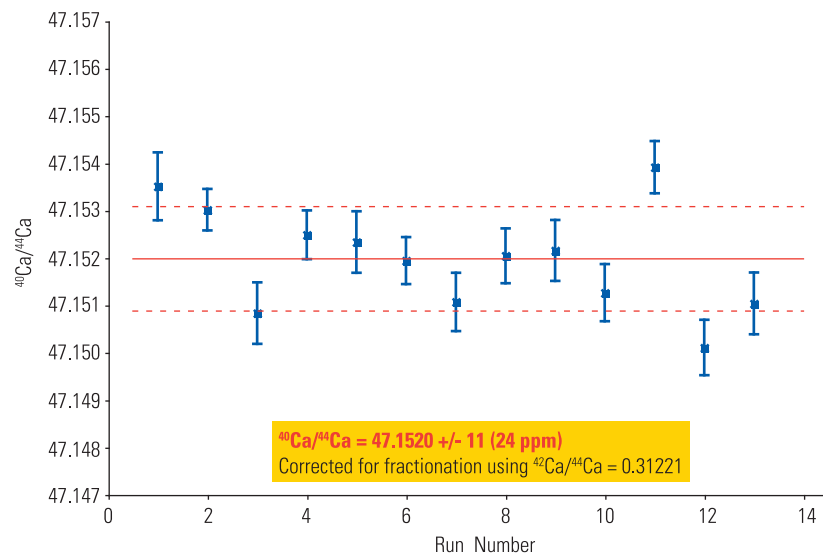
$^{44}\text{Ca} \rightarrow 0.95 \text{ V}$



Emission Profile of a Typical Run

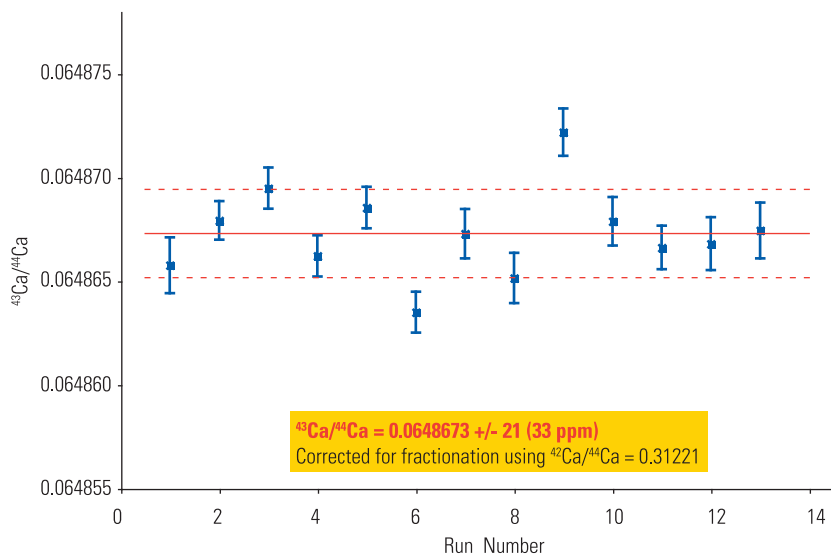


Results and Summary



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

Results and Summary continued



⁴³Ca/⁴⁴Ca - External reproducibility

- Thermo Scientific TRITON's increased dynamic range allows Ca-measurements at intensities up to 50 Volt without resistor change of current amplifiers
- **Intensities for ⁴⁰Ca 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 ⁴⁶Ca and ⁴⁸Ca together with ⁴⁴Ca 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 (1σ _E) (AVERAGE) |
|------------------------------------|--------------|---------------------------------------|
| ⁴⁰ Ca/ ⁴⁴ Ca | 24 ppm | 13 ppm |
| ⁴³ Ca/ ⁴⁴ Ca | 33 ppm | 18 ppm |

Fractionation corrected by "Exponential Law" using ⁴²Ca/⁴⁴Ca = 0.31221

References

- Russell, W.A., Papanastassiou, D.A. and Tombrello, T.A., 1978, Ca isotope fractionation on the Earth and other solar system materials. *Geochimica et Cosmochimica Acta*, Vol. 42, p. 1075-1090
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