

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

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## 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 ( $2\sigma$ ); 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 Finnigan™ 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 Finnigan TRITON ensures precise and accurate analyses.

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

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 25ppm ( $1\sigma$ ), approaching theoretical limits.

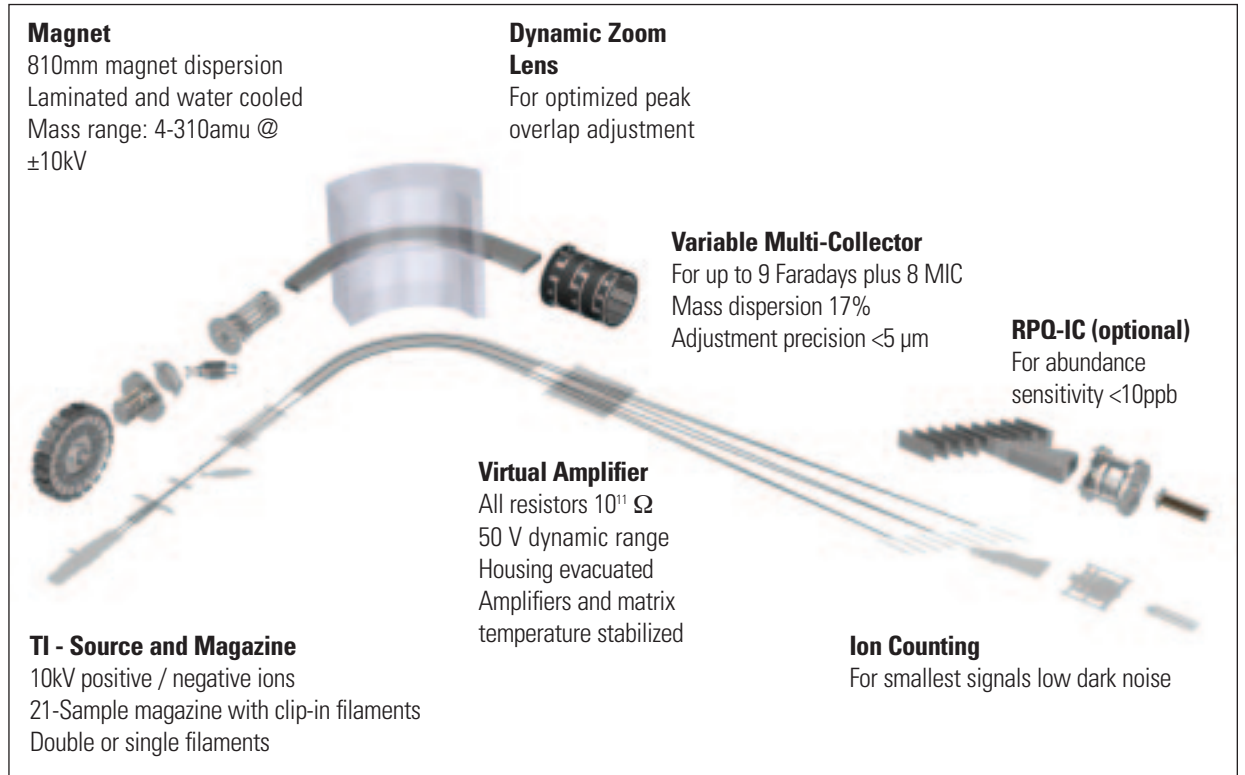
## Key Words

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



Thermal Ionization Mass Spectrometer Finnigan TRITON

## Experimental



## Sample and Analysis Parameter

### Sample:

CaCO<sub>3</sub> (Laboratory Standard) in 1% HNO<sub>3</sub>  
Concentration: 1μg/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 1.5A, then 30 sec. at 2.0A

### MS-Condition:

Accelerating Voltage: 10000 Volt, positive  
Ion source vacuum: < 2 x 10<sup>-7</sup> mbar  
Analyzer vacuum: < 2 x 10<sup>-9</sup> mbar  
Amplifier Resistors: 10<sup>11</sup> Ω,  
Stability: < 10μV / h  
Amplifier gains: Gs < 10ppm / day,  
Virtual Amplifier rotation

### Sample Heating:

Ionization Fil. to 2900-3100mA within 10 minutes  
Evaporation Fil. about 400mA within 10 minutes  
Target signal: 45 Volt @ <sup>40</sup>Ca

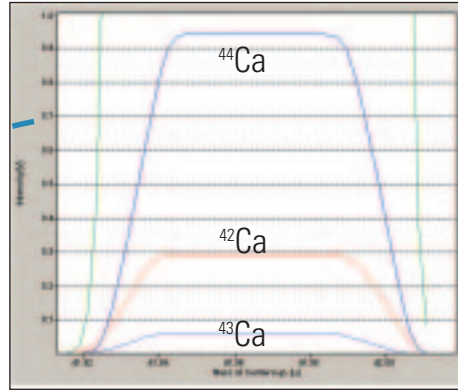
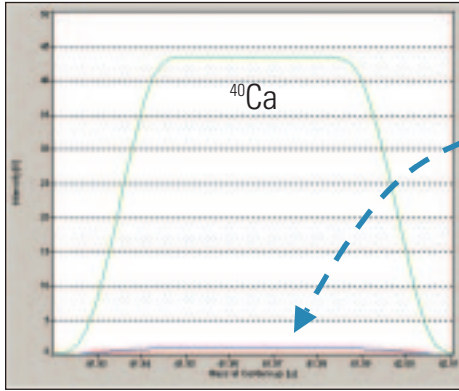
### Data Collection:

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

## Setup of Faraday Cups for Ca Measurement



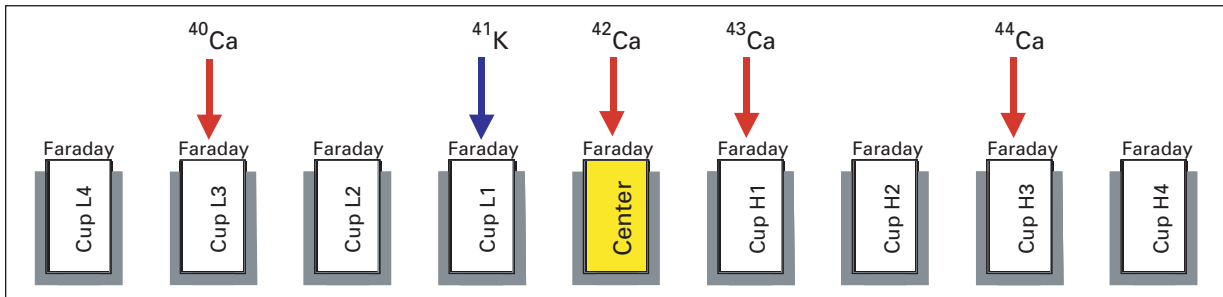
### Ca-Intensities @ $10^{11} \Omega$ :

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

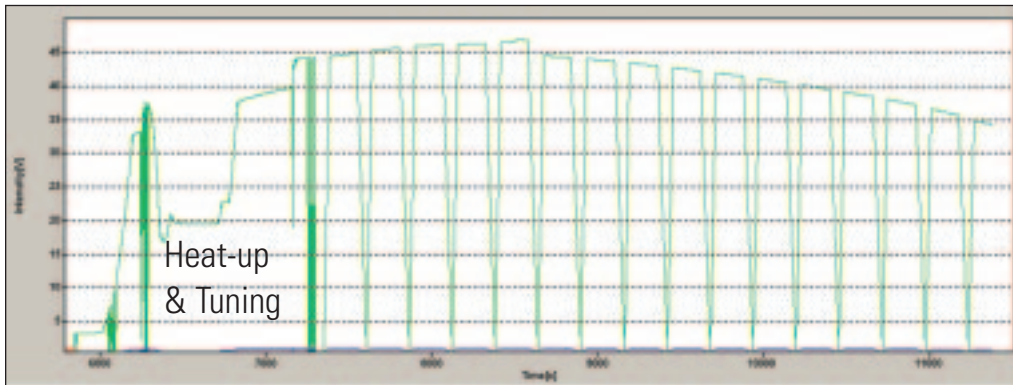
$^{42}\text{Ca} \rightarrow 0.3 \text{ V}$

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

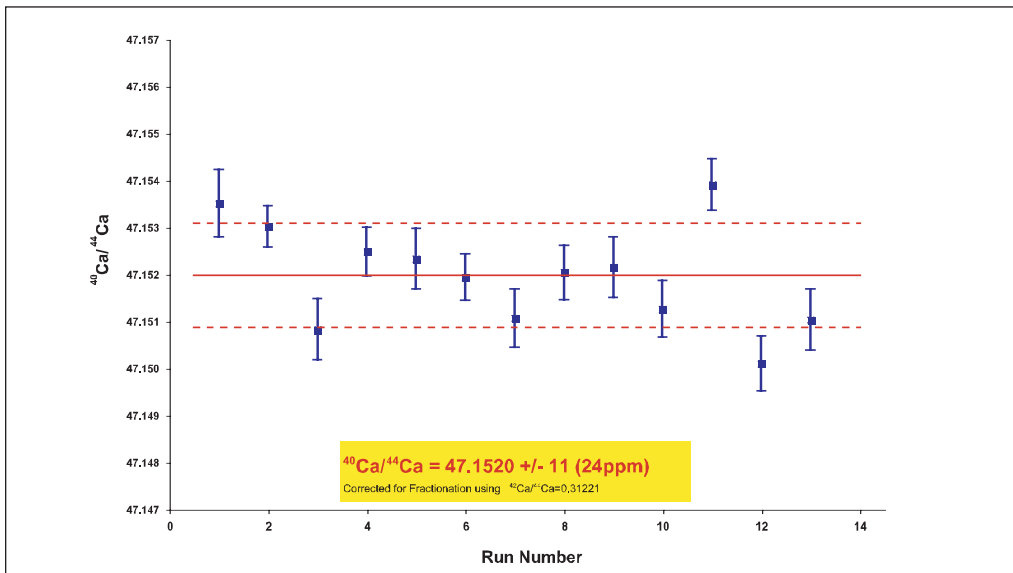
$^{44}\text{Ca} \rightarrow 0.95 \text{ V}$



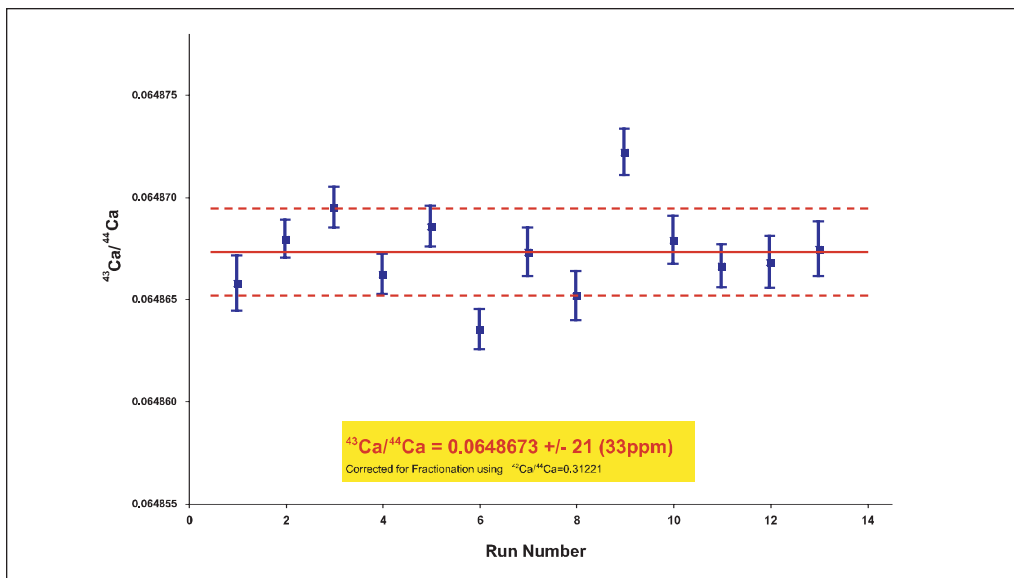
## Emission Profile of a Typical Run



## Results and Summary



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



<sup>43</sup>Ca/<sup>44</sup>Ca - External reproducibility

- Finnigan TRITON's increased dynamic range allows Ca-measurements at intensities up to 50 Volt without resistor change of current amplifiers  
**Intensities for <sup>40</sup>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 <sup>46</sup>Ca and <sup>48</sup>Ca together with <sup>44</sup>Ca in a 2nd step
- In contrast to ICP-MS, TI-MS can be used to measure <sup>40</sup>Ca directly with highest precision in static mode without any interference correction
- Achieved precisions are:

	EXTERNAL(1σ)	INTERNAL (1σ <sub>E</sub> ) (AVERAGE)
<sup>40</sup> Ca/ <sup>44</sup> Ca:	24 ppm	13 ppm
<sup>43</sup> Ca/ <sup>44</sup> Ca	33 ppm	18 ppm

Fractionation corrected by "Exponential Law" using <sup>42</sup>Ca/<sup>44</sup>Ca = 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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