

Do we have a choice of reaction gas for measuring Ca? Investigations using the Thermo Scientific Neoma MS/MS MC-ICP-MS

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Abstract

High precision measurements of the Ca isotope system have always been challenging, due to the wide range of natural abundances for its six naturally occurring nuclides and the high number of potential interferences. Most obviously for those wishing to use multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for Ca isotopic measurements is the isobaric overlap between $^{40}\text{Ar}^+$, the single largest component of the ICP, and $^{40}\text{Ca}^+$. MC-ICP-MS has for some time been used to measure $^{42}\text{Ca} - ^{48}\text{Ca}^1$; but it is only in the last few years, with the re-introduction of collision/reaction cell technology to MC-ICP-MS, that it has been possible to report $\delta^{44}\text{Ca}$ with MC-ICP-MS^{2,3}, instead of a double spike TIMS method. The addition of H_2 gas (alongside He) to the collision/reaction cell neutralizes the $^{40}\text{Ar}^+$ ions to $^{40}\text{Ar}^0$, allowing the $^{40}\text{Ca}^+$ to be measured interference free.

However, there is another potential mechanism to measure $^{40}\text{Ca}^+$ free from $^{40}\text{Ar}^+$ with a MC-ICP-MS. Like its fellow alkaline earth element Sr^4 , Ca^+ ions readily react with SF_6 in a collision/reaction cell to form CaF^+ . SF_6 has the potential to eliminate not only the $^{40}\text{Ar}^+$ interference on $^{40}\text{Ca}^+$, but also the interference of $^{88}\text{Sr}^{++}$ on $^{44}\text{Ca}^+$. This opens the possibility of measuring high precision Ca isotopic ratios in-situ for solid samples via laser ablation MC-ICP-MS. Here we report our investigations into using SF_6 as a reaction gas for high-precision calcium isotopic ratio measurements with a Thermo Scientific™ Neoma™ MS/MS MC-ICP-MS for both solution and solid samples.

Introduction

Multicollector inductively coupled plasma mass spectrometry has been used to precisely measure the isotopic composition of calcium for over a decade. However, with collision/reaction cells absent from commercially available MC-ICP-MS for many years, most often ^{40}Ca could not be measured, due to the isobaric interference from the ^{40}Ar , which is in overwhelming concentration within the ICP. As MC-ICP-MS equipped with collision/reaction cells have become more widely available, the measurement of high precision Ca isotope ratios including $^{40}\text{Ca}/^{44}\text{Ca}$, has been increasingly popular.

The easiest method to measure $^{40}\text{Ca}^+$ free from $^{40}\text{Ar}^+$ is via the introduction of H_2 and He into the collision/reaction cell. The H_2 reacts with the $^{40}\text{Ar}^+$, neutralizing it to $^{40}\text{Ar}^0$, but not affecting $^{40}\text{Ca}^+$. This method has been shown repeatedly, in numerous publications, to be accurate, precise and repeatable. However, $^{40}\text{Ar}^+$ is not the only major interferent on Ca nuclides, another major interferent is $^{88}\text{Sr}^{++}$ on $^{44}\text{Ca}^+$. As both Sr and Ca are rare-earth elements, they are often found together in high concentrations in the same minerals. The reaction gas SF_6 , is already well known to readily react with Sr to SrF^+ , and the same is true of Ca, forming CaF^+ . The reaction of Ca to CaF^+ has the potential to move the Ca nuclides away from both interferences, $^{40}\text{Ar}^+$ and $^{88}\text{Sr}^{++}$, weakening the reliance on column chemistry and potentially allowing in-situ analysis of the Ca isotopic composition by laser ablation.



Method

For the analysis, 1000 ng/g Ca in 0.5 M HCl solutions were made for the NIST SRM915b reference material and four sample materials. The sample materials were named HPS, Tritisol, SW and EN-1. All four samples except EN-1 were expected to be pure. The sample of EN-1 measured had, in addition to Ca, 400,000 ng/g of Sr. Ten, 5-minute replicate measurements, consisting of 75 repeats of 4 second integration time, were made for HPS, Tritisol and SW. Only four replicate measurements were made of EN-1 due to the high matrix in the sample.

The Neoma MS/MS MC-ICP-MS used was equipped with three $10^{13} \Omega$ amplifiers and a single, axial, secondary electron multiplier (SEM). A $10^{13} \Omega$ amplifier, which extends the operational range of the Faraday cup detector to lower values compared to the $10^{11} \Omega$ amplifier was used to measure ^{46}Ca (Table 1). The Jet interface, combining a high efficiency interface pump with X skimmer and Jet sampler cones, was used to maximize sensitivity. All blanks, standards and samples were aspirated at an uptake rate of approximately 100 $\mu\text{L}/\text{min}$ via an ESI@Apex Omega™ Q desolvating nebulizer system. The argon sweep gas of the Apex Omega was 2.00 L/min and the additional nitrogen flow was 5.0 mL/min. Medium resolution was used.

Table 1. Cup configuration and amplifier assignment for CaF on the Neoma MS/MS MC-ICP-MS.

Cup	L5	L4	L3	L2	L1	C	H1	H2	H3	H4	H5
CaF	^{40}CaF		^{42}CaF		^{43}CaF	^{44}CaF	^{46}CaF			^{48}CaF	
Amplifier	$10^{11} \Omega$		$10^{11} \Omega$		$10^{11} \Omega$	$10^{11} \Omega$	$10^{13} \Omega$			$10^{11} \Omega$	

The prefilter of the Neoma MS/MS was tuned to fully transmit all the Ca nuclides, but to not transmit any nuclide of 59 m/z or greater. This was achieved by tuning with a solution which contained both calcium and cobalt (m/z 59). A magnetic field strength of 20% of the maximum applied current was sufficient (Table 2). Once the window had been selected with the Prefilter, the Ca nuclides were reacted to CaF^+ by the addition of SF_6 and He to the collision/reaction cell (Table 3).

Table 2. Prefilter settings of the Neoma MS/MS MC-ICP-MS.

Prefilter		
Magnetic field	%	20
Electric field	V	159
L1 base	V	-460
L1 X-symmetry	V	-2
L1 Y-symmetry	V	-12
L2 base	V	-456
L3 base	V	-340
L3 X-symmetry	V	0
L3 Y-symmetry	V	11

Table 3. Collision/reaction cell settings of the Neoma MS/MS MC-ICP-MS. The SF_6 was introduced using a MFC calibrated for NH_3 .

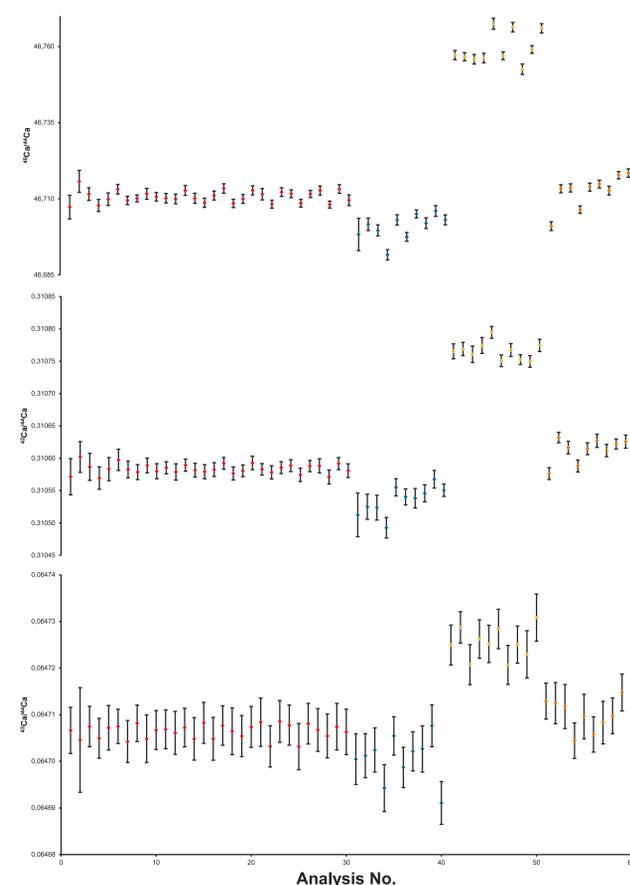
Collision/Reaction Cell	
CCT entry	V -42.5
CCT bias	V -3.5
RF amplitude	% 100
CCT exit 1	V -110
CCT exit 2	V -80
MFC1 He	mL/min 1.3
MFC3 SF_6	mL/min 0.07

For laser ablation, the Neoma MS/MS MC-ICP-MS was coupled to an ESL™ NWR™ imageGEO™ 193 nm excimer laser ablation system equipped with the TV3™ ablation cell. Samples measured were the reference glasses SRM614 and BH4O-2G and the apatites Durango, Madagascar, SUME and iPIRA. The reference glass SRM610 was used as the standard. However, as the Ca isotopic composition of SRM610 could not be found in literature, it was arbitrarily assigned the Ca isotopic composition given by UIPAC.

Every sample was ablated for 60 seconds at a fluence of 5 J/cm^2 and a repetition rate of 10 Hz. Every material was ablated for 60 second spot ablation was used with a 1 second. To compensate for the lower Ca abundance in the glasses, these were ablated with a larger spot size, 100 μm , compared to the apatites, 50 μm .

All data processing, both solution and solid, was performed in Iolite 4 using a custom-made CaF Neoma data reduction scheme, which the authors would make available on request.

Figure 1. $^{40}\text{Ca}/^{44}\text{Ca}$, $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$, measured as CaF, of SRM915b (red), HPS (purple), SW (yellow) and Tritisol (orange).



Results

Compared to using H and He as the reaction gas mixture, SF_6 and He reduced the sensitivity by a factor of five. Consequently, a higher sample concentration of Ca was required for the solution-based sample materials. Measurement of ^{46}Ca and ^{48}Ca were also impaired by the presence of large, molecular interferences. These interferences were identified as likely being $^{32}\text{S}^{19}\text{F}^{14}\text{N}^+$ and $^{32}\text{S}^{19}\text{F}^{16}\text{O}^+$ respectively.

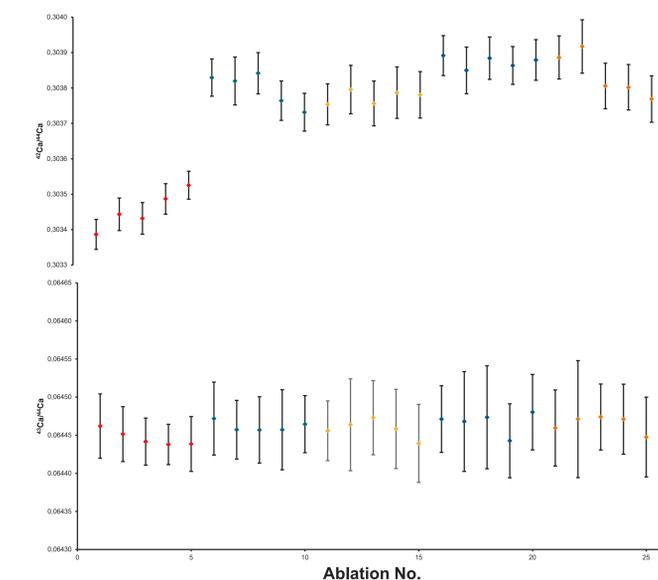
Perhaps unexpectedly, the reproducibility of $^{40}\text{Ca}/^{44}\text{Ca}$ was worse than for $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$, which does not correlate with the significantly higher sensitivity of ^{40}Ca compared to the minor isotopes (Figure 1). For Tritisol the results were $\delta^{42}\text{Ca} = 0.095 \pm 0.056 \text{‰}$, $\delta^{43}\text{Ca} = 0.055 \pm 0.052 \text{‰}$ and $\delta^{40}\text{Ca} = 0.036 \pm 0.108 \text{‰}$, relative to SRM915b. SW returned values of $\delta^{42}\text{Ca} = 0.586 \pm 0.048 \text{‰}$, $\delta^{43}\text{Ca} = 0.290 \pm 0.047 \text{‰}$, $\delta^{40}\text{Ca} = 1.041 \pm 0.109 \text{‰}$ and for HPS $\delta^{42}\text{Ca} = -0.160 \pm 0.067 \text{‰}$, $\delta^{43}\text{Ca} = -0.087 \pm 0.076 \text{‰}$, $\delta^{40}\text{Ca} = -0.216 \pm 0.086 \text{‰}$.

For EN-1, which contained the high concentration of Sr, high matrix effects in the ICP were observed, affecting reproducibility. However, the measured values were in the expected range for this material, which suggested some cause for optimism when it came to measuring solid samples.

The $^{40}\text{Ca}/^{44}\text{Ca}$, $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$ for all glasses and apatites were broadly consistent (Figure 2), apart from BHVO-2G. BHVO-2G had the lowest measured concentration of Ca, about 1/10th of the other material, which likely contributed to the shift.

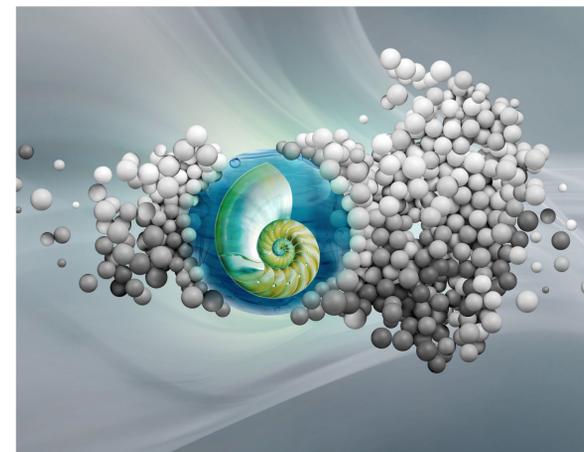
The uncertainty measured for $^{42}\text{Ca}/^{44}\text{Ca}$ varied from 0.11 ‰ (2RSD, SUME) to 0.41 ‰ (2RSD, SRM614) For $^{43}\text{Ca}/^{44}\text{Ca}$ the uncertainty ranged from 0.20 ‰ (2RSD, Madagascar) to 0.45 ‰ (2RSD, SUME).

Figure 2. $^{42}\text{Ca}/^{44}\text{Ca}$ and $^{43}\text{Ca}/^{44}\text{Ca}$, measured as CaF, of SRM614 (red), Madagascar (purple), Durango (yellow), SUME (blue) and iPIRA (orange).



Conclusions

The Neoma MS/MS MC-ICP-MS has the potential to allow in-site Ca isotope ratio analysis via the use of SF_6 as a reaction gas. However, the higher sensitivity, better precision and lesser interferences on ^{46}Ca and ^{48}Ca make H_2 the superior reaction gas for solution-based analysis.



References

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