Precise Calcium Isotope Determination with the Sapphire Dual-Path MC-ICP-MS

Calcium (Ca) isotopes in primitive meteorites and rocks from Earth, the Moon, and Mars can be used to provide information on early solar system processes and planetary differentiation. High precision Ca isotopic measurements are often performed on the Multi-collector ICP-MS (MC-ICP-MS) due to its high ionization efficiency and fast sample throughput. However, this technique is limited by the presence of the large $^{40}Ar^{+}$ ion beam which prevents the measurement of $^{40}Ca^{+}$. Ar-based polyatomic species such as $^{40}ArH_2^{+}$ also interfere on other Ca isotopes and need to be resolved using high mass resolution. In addition, there can be baseline scattering contributed by the large $^{40}Ar^{+}$ beam.

Figure 1: The Sapphire

In this study, the Nu Sapphire, a novel MC-ICP-MS instrument equipped with a dual-path design (Figure 2) including both a conventional MC-ICP-MS (high-energy) path and a hexapole collision cell (low-energy) path, is used for Ca isotopic measurements. Following extraction of the ions from the ICP at 6 kV, the ions are deflected off-axis and decelerated to enter the collision cell. In the cell, the ions mix with He and H_2 gases to remove interfering species and are then re-accelerated to 6 kV on exiting the cell and focused back onto the high-energy path.

Two NIST standard solutions 915a and 915b were measured against each other in this study. Solution was introduced into the mass spectrometer in 0.3% HNO_3 under 'dry plasma' conditions, using an Apex Omega Desolvating Nebuliser system with a PFA nebuliser with a 0.16 ml/min uptake rate and the Enhanced Sensitivity (ES) interface (see Nu Plasma Application Note NP05). 3 sccm He and 6 sccm H_2 were used in the cell to remove Ar based interferences.

Data was collected in static mode, with $^{40}Ca^{+}$ measured in a Faraday cup (L4 in Table 1) connected to a pre-amplifier fitted with a 10^{10} ohm resistor and the rest using 10^{11} ohm resistors. 10 repeated analyses of the 915b standard were bracketed with the 915a standard. Each measurement consisted of one block of 50 cycles of 5 sec integration. Each measurement was preceded with a 1 min 'on peak' blank measurement of a 0.3% HNO_3 solution and followed by a 3 min wash. No tuning of the instrument or nebuliser was made once the measurement batch had started.

Mass 43.5 was simultaneously monitored for $^{87}Sr^{2+}$ to correct for the unresolvable isobaric interferences of $^{84}Sr^{2+}$ on $^{42}Ca^{+}$, $^{86}Sr^{2+}$ on $^{43}Ca^{+}$ and $^{88}Sr2^{+}$ on $^{44}Ca^{+}$ (Table 1).

Collector	H9	H8	H7	X	H6	X	H5	H4	H3	H2	H1	Ax	L1	L2	L3	X	L4
Isotope	$^{88}Sr^{2+}$ $^{44}Ca^{+}$		$^{87}Sr^{2+}$		$^{86}Sr^{2+}$ $^{43}Ca^{+}$				$^{84}Sr^{2+}$ $^{42}Ca^{+}$								$^{40}Ca^{+}$

Table 1: Sapphire cup configuration used in this study. Grey represents Faraday cups, yellow dummy cups. Ca isotopes are in green, Sr isotopes are in blue. The collector array also includes 6 ion counters, 2 additional Faraday cups and 2 additional dummy cups.

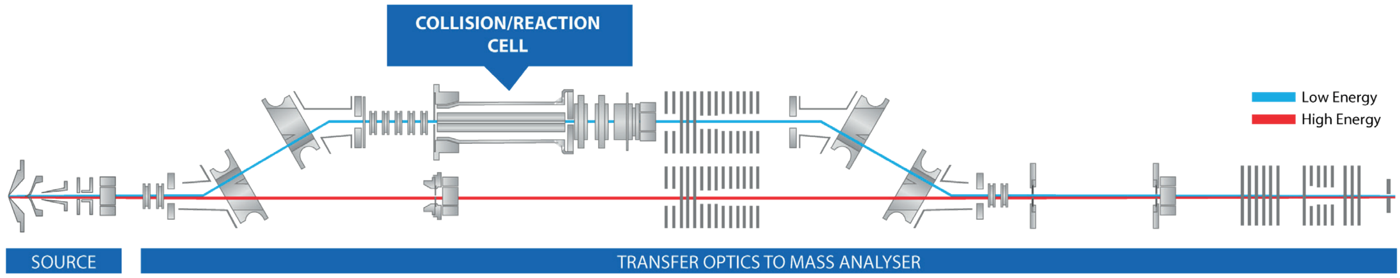

Figure 2: Dual-path design on the Sapphire (UK Patent GB2535826). Red line represents the conventional MC-ICP-MS (high energy) path, blue line represents the collision cell (low energy) path.

sapphire

The Ca sensitivity achieved was approx. 1,000 volts/ppm. The Ca blank was less than 1 ppb.

To correct for the doubly charged Sr interferences, a fractionation factor of -1.6 was used to calculate the $^{84}Sr^{2+}$, $^{86}Sr^{2+}$, $^{88}Sr^{2+}$ from $^{87}Sr^{2+}$ using the Exponential Law. The obtained $^{40}Ca/^{44}Ca$ of 915a and 915b are plotted in Figure 3. The linear drift of the ratio was related to the signal drop caused by coating of Ca on the skimmer cone during the sequence.

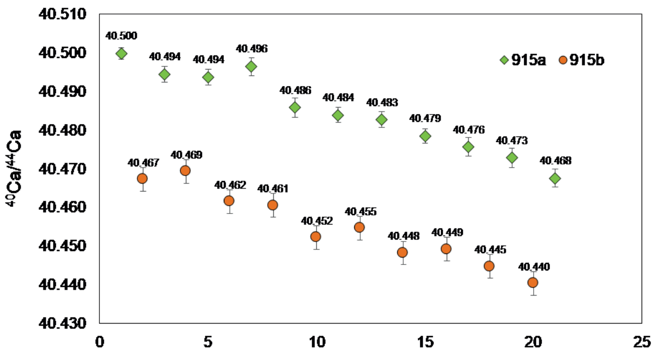

Figure 3: $^{40}Ca/^{44}Ca$ results of the NIST 915a and 915b standards measured using the Sapphire collision cell.

The obtained $\delta^{40}Ca$, $\delta^{42}Ca$ and $\delta^{43}Ca$ values of the 915b standard are reported in Table 2. The $\delta^{40}Ca$ is in good agreement with the published TIMS value of -0.72 ± 0.04‰[1].

SSB Brackets (n)	Ratio	SD (‰)	2 SD (‰)	Mass bias (per amu)
10	$^{40}Ca/^{44}Ca$	-0.74	0.12	3.7%
	$^{42}Ca/^{44}Ca$	-0.34	0.06	
	$^{43}Ca/^{44}Ca$	-0.14	0.10	

Table 2: Ca isotopic results of 915b against 915a using the Sapphire collision cell.

The Ca isotopic results demonstrate in detail the capability of the Nu Sapphire dual-path MC-ICP-MS to provide accurate and precise Ca isotopic data. The collision cell greatly benefits high precision Ca isotopic measurements, as the technique enables efficient removal of Ar-based spectral interferences. This technique not only makes the direct measurement of $^{40}Ca^{+}$ possible, but also avoids the need to use high resolution, reducing the sample size by an order of magnitude.

Reference

[1] Heuser, A., Eisenhauer, A., 2008. The calcium isotope composition ($\delta^{44/40}Ca$) of NIST SRM 915b and NIST SRM 1486. Geostand. Geoanal. Res. 32 (3), 311–315.