sapphire

Highly Precise and Accurate Potassium Isotope Determination

Among moderately volatile and relatively abundant elements, only potassium (K) has more than one stable isotope (^{39}K and ^{41}K), making it a good candidate for studying the history of volatile element depletion in the early Solar System[1]. High precision K 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 $^{40}ArH^+$ ion beam which restricts/complicates the measurement of $^{41}K^+$. This large beam needs to be resolved and supressed using high mass resolution in the cold plasma mode. In addition, there can be baseline scattering contributed by the very large $^{40}Ar^+$ beam.

In this study, the Nu Sapphire (SP001) installed at the Department of Earth and Planetary Sciences, Harvard University was used for the K isotope measurements. The Nu Sapphire, is a novel MC-ICP-MS instrument equipped with both a conventional MC-ICP-MS (high-energy) path and a hexapole collision cell (low-energy) path. For the low-energy path, following extraction of the ions from the ICP at 6 kV, the ions are 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.

A lab standard, Merck Suprapur (KNO_3 of 99.995% purity) and a USGS BHVO-2 standard were used in this study. Solution was introduced into the mass spectrometer in 2% HNO_3 under 'dry plasma' conditions, using an Apex Omega Desolvating Nebuliser system with a PFA nebuliser with a 0.1 ml/min uptake rate and the Enhanced Sensitivity (ES) interface (see Nu Instruments Application Note AN27). 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 $^{39}K^+$ measured in a Faraday cup (L4 in Table 1) connected to a pre-amplifier fitted with a 10^{10} ohm resistor and $^{41}K^+$ using a 10^{11} ohm resistor Faraday cup (H3 in Table 1). The BHVO-2 was analysed repeatedly against the Suprapur standard. Each measurement consisted of one block of 15 cycles of 5 seconds integration. The measurement sequence was preceded with a 1 min 'on peak' zero measurement in 2% HNO_3, and each measurement was followed by a 10 second wash in 2% HNO_3. No tuning of the instrument or nebuliser was made once the measurement sample batch had started.

The collector configuration is displayed in Table 1. The typical peak alignment is displayed in Figure 1.

Table 1 displays the Sapphire collector configuration used in this study. Blue and green represent Faraday cups, yellow dummy cups. The collector array also includes 1 additional Faraday cup and 4 ion counters – not shown below.

Collector	H10	X	H9	H8	H7	X	H6	X	H5	H4	H3	H2	H1	Ax	L1	L2	L3	X	L4
Isotope											$^{41}K^+$				$^{40}K^+$				$^{39}K^+$

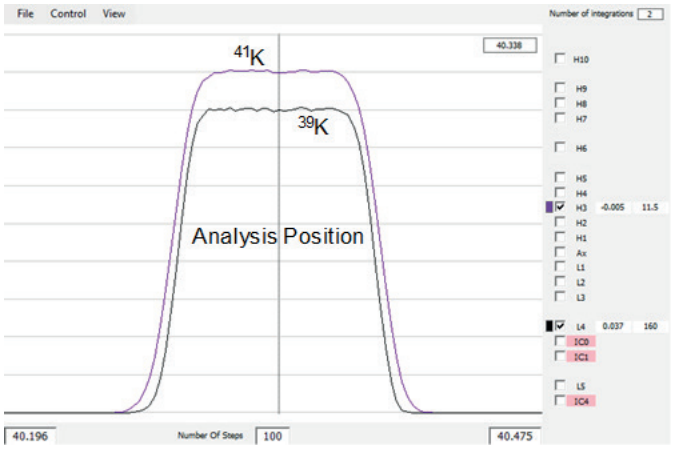

Figure 1: K isotopes ^{39}K and ^{41}K in coincidence. The centre of the flat peaks was chosen as the mass analysis position.

The achieved K sensitivity was approximately 1,300 volts/ppm and the entire sequence lasted 12 hours. The $\delta^{41/39}K$ of the Suprapur standard bracketing itself are plotted in Figure 2. The typical internal precision is 0.015‰ (2 RSE), the average $\delta^{41/39}K$ is -0.001 ± 0.006 (2σ, n=20).

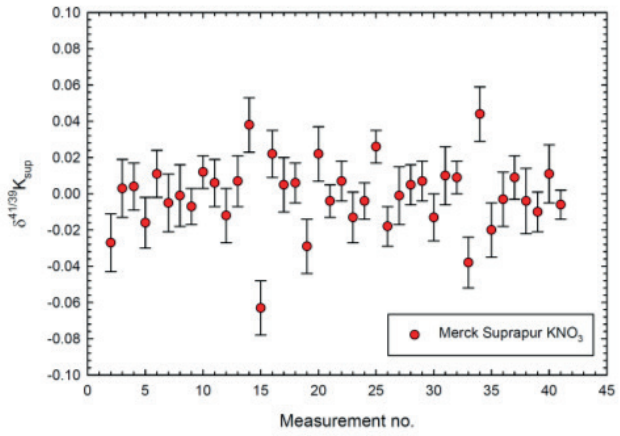

Figure 2: $\delta^{41/39}K$ results of the Suprapur standard bracketing itself in a 12 hour sequence. Error bars are 2 SE.

The measurements of BHVO-2 relative to the Suprapur were repeated on different days, and the $\delta^{41/39}K$ value from each day is reported in Figure 3. The average $\delta^{41/39}K$ = -0.334 ± 0.007 (2σ, n = 9).

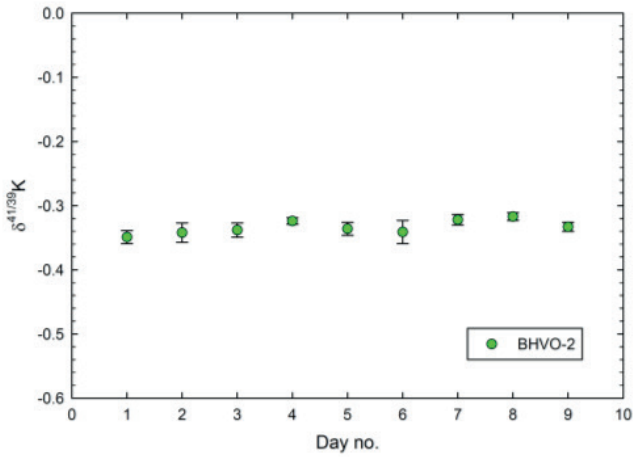

Figure 3: $\delta^{41/39}K$ results of the repeat measurements of the BHVO-2 against the Suprapur on 9 different days. Each data point represents the mean $\delta^{41/39}K$ value obtained on that day.

The experiment demonstrates in detail the capability of the Nu Sapphire dual-path MC-ICP-MS to provide highly accurate and precise K isotopic data. The collision cell enables efficient removal of Ar-based spectral interferences, which makes the direct measurement of $^{41}K^+$ in low resolution possible, reducing the sample size by an order of magnitude compared to measurements performed using high resolution. This allows the analysis of samples with very low K concentrations or tiny aliquots of extremely precious samples such as meteorites and lunar rocks.

Acknowledgements

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References

[1] Y. Ku and S. B. Jacobsen, 2019. Potassium isotope variations in Chondrites. 50th Lunar and Planetary Science Conference 2019 (LPI Contrib. No. 2132)