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Plasma Note **NP06**

High Precision Determination of Potassium Stable Isotope Ratios

Introduction

Potassium (K) is an important element in various metabolic and physiological processes. K stable isotopes "K and ''K are of broad interest in weathering studies, nutrient cycling studies, plant growth studies and human cardiovascular system studies. The measurements of K stable isotope compositions, however, have been known to be very difficult. Traditional TIMS measurements are hindered by variable fractionation patterns and too few isotopes being available to correct for instrumental mass fractionations internally. MC-ICP-MS analyses are significantly affected by instrumental mass fractionations and interferences from molecular species such as ^{40}ArH, ^{38}ArH. Moreover, as a result of the chemistry of K in the terrestrial environment, terrestrial materials are reported to have very small K isotopic variations ($\delta^{41}/^{39}K_{terrestrial}$= 0.28 ± 0.21‰, 2σ; Humayun and Clayton[1]), which would require high-precision isotopic measurements to resolve.

Results of potassium isotopic measurements using the Nu Plasma II instrument, performed on the interference-free shoulders of ^{39}K and ^{41}K, at Pseudo-High Resolution mode with a lower RF Forward Power are presented in this note. The high precision presented, indicates the potential for the Nu Plasma II instrument to determine K isotopic variations at the sub-per mil level.

Instrumentation

In the experiment, a 4 ppm solution of the Spex Certiprep K standard has been used. The solution was introduced into the mass spectrometer under 'dry plasma' conditions, using a DSN-100 Desolvating Nebuliser System with a 100 µL/min glass concentric nebuliser and standard cones.

Nu Plasma II

One major analytical difficulty of K isotopic measurement via MC ICP-MS comes from the intense background of ^{40}Ar. A collector configuration shown in Table. I has been used so that the ^{40}Ar beam was collected by the dummy bucket located between Faraday cups H? and H8. Clean baselines were achieved on HS and H9.

Another major analytical difficulty is the isobaric interferences of ^{40}ArH on 41K, and ^{38}ArH on ^{39}K. The '"ArH interference was negligible in this study. Using the standard Forward Power of 1300 W, the ^{40}ArH/^{41}K ratio was high and a tailing effect of ^{40}ArH was observed on ^{41}K, which would affect the measured isotope ratios. It was known that reducing the Forward Power can significantly suppress the formation of ^{40}ArH molecules, a lower Forward Power was therefore desirable. A test was performed to investigate the relationship between Forward Power and ^{40}ArH/^{41}K ratio. The instrument was re-tuned every time the Forward Power was changed. It is worth mentioning, although the tuning of the instrument should normally aim for the maximum beam intensity, in this very case the maximum beam intensity did not correspond to the flattest resolved analyte shoulder. A flat analyte shoulder is crucial for high-precision isotopic measurements. Therefore, the tuning aimed for a balance between the analyte shoulder flatness and beam intensity instead.

As Table 2 suggests, ^{40}ArH/^{41}K had a minimum value of 0.3 when the Forward Power was reduced to I050 W, beyond which no significant decrease in the ratio was observed. To avoid further loss of beam intensities, a Forward Power of I 050 W was used in this study. The sensitivity decreased by ca. 50% when the Forward Power was reduced from I300 W to I050 W.

Data was collected using static analysis. Each analysis consisted of two blocks of 25 integrations of 5 s on-peak measurements of K, baselines were obtained by ESA deflection at the start of each block. Each analysis took 5 minutes. 21 repeat analyses were made, equating to ca. 2 hours of data collection. No tuning of the instrument or nebuliser was made once the measurements had started. Measurements were carried out on the interference-free shoulders of the ^{41}K, ^{39}K peaks, in the Pseudo-High Resolution mode (30 IJm source defining slit, high resolution) with a resolving power of approximately 14,400 (5, 95% Edge Resolving Power, for definition please refer to AN22) Instead of bringing the edges of ^{41}K, ^{39}K into coincidence, the ^{41}Kedge was moved further in to ensure a better overlap of the two interference-free analyte shoulders (Figure I).

Collector	HMIC	H9	X	X	H8	X	H7	X	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	IC0	L5	IC1	IC2	L6	IC3	X	IC4
Position	-14	-13	-12	-11	-10	-9	-8	-7	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8	9	10	11	12
K		41								39																	

Table 1: Nu Plasma II collector configuration for the static measurement of potassium isotopes.

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Forward Power (W)	1300	1250	1200	1150	1100	1050	1000	950
^{40}ArH/^{41}K	4.8	3.3	3	1.8	1.3	0.3	0.3	0.3

Table 2: Test results of Forward Power (0N) versus ^{40}ArH/^{41}K.

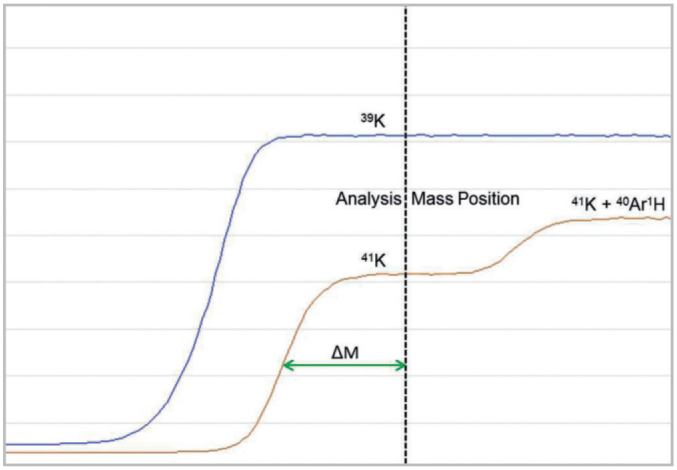

Figure 1: Potassium isotope ^{41}K partially resolved from its major interference ^{40}ArH in the Pseudo-High Resolution mode using the 30 m source defining slit.

As a result of the high resolving power (4887, I 0% valley Resolving Power, for definition please refer to AN22) required to partially separate the analyte from interferences, the resolved ''K shoulder was quite narrow. The isotopic measurement precision was, therefore, sensitive to the selected analysis mass position. A test of the impact of different ΔM (definition see Fig. I) values on the internal precision is displayed in Table 3 A ΔM = 0.0061 was used for the isotopic measurement in this study since an optimal internal precision was achieved at this analysis mass position.

Discussion

A 'sample-calibrator bracketing' method has been used for the isotopic measurement, results are being shown in Table 4, where δ denotes the per mil deviation of the measured ^{41}K/^{39}K ratio relative to the average of the two ratios measured before and after.

The measured $\delta^{41}/^{39}$K = 0.043 ± 0.14‰ (2σ) are close to the expected O‰ and the external precision is comparable to what has been achieved on a different MC-ICP-MS instrument (σ 0.07‰; Morgan et al.[2]).

A sensitivity of 3.5 volts/ppm for total potassium was achieved in the Pseudo-High Resolution mode. No internal mass fractionation correction has been applied to the measured potassium isotopic data (Figure 2). The measured ^{41}K/^{39} K ratios show a ca. 9% instrumental mass fractionation.

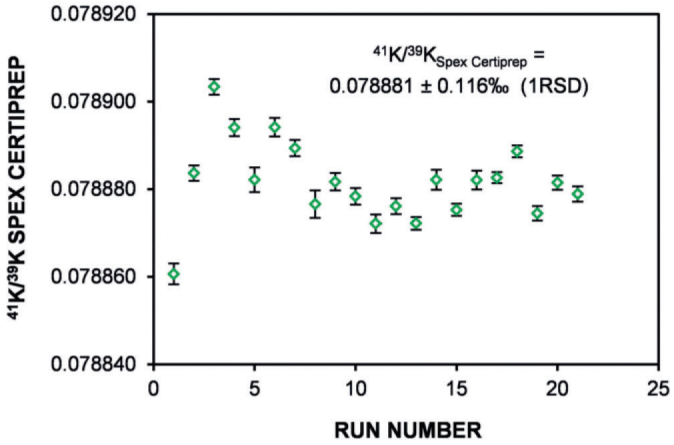

Figure 2: ^{41}K/^{39}K ratios of the 4 ppm Spex Certiprep K standard solution measured over the course of 2 hours. Error bars are 2SE.

Although no internal mass fractionation correction was available, this fractionation was sufficiently stable over the time required for a number of analyses therefore a sample-standard bracketing method is suitable to be used to correct for the instrumental mass fractionation.

Conclusion

The Nu Plasma II Multi Collector ICP-MS instrument has been demonstrated to exhibit high precision in determining potassium stable isotope ratios.

Forward Power (W)	0.0039	0.0042	0.0046	0.0049	0.0053	0.0055	0.0058	0.0061	0.0064	0.0067
RSE (ppm)	1308	634	871	355	35	31	28	19	21	25

Table 3: Test results of RSE (ppm) versus M.

	^{41}K/^{39}K
Average δ (‰)	0.043
SD (‰)	0.068

Table 4: 'Sample-calibrator bracketing' results of 21 repeated analyses of a 4 ppm Spex Certiprep K standard solution .

Reference

[1] Humayun, M. and Clayton, R.N., 1995. Potassium isotope cosmochemistry: Genetic implications of volatile element depletion. Geochim. Cosmochim. Acta 59, 2131-2148.

[2] Morgan, L E., Lloyd, N S., Ell am, R M., Simon,J 1., Higgins, J., 2013. Potassium stable isotopic compositions measured by high resolution MC-ICP-MS. Goldschmidt meeting, 2013.