

Significantly Enhanced Robustness of K Isotope Analysis by Collision Cell MC-ICP-MS and Its Application to the Returned Lunar Samples by China's Chang'e-5 Project

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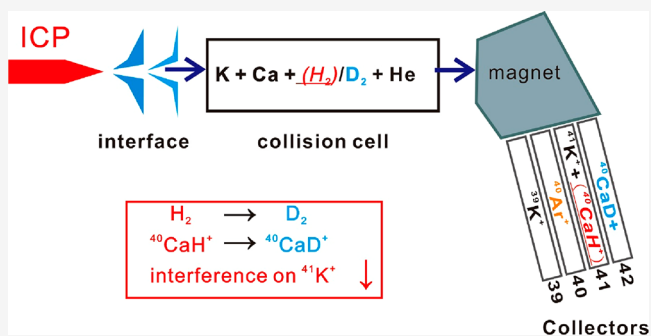
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ABSTRACT: Stable K isotope ratios, an emerging research tool for a wide range of problems, can be measured precisely with high sensitivity by using collision cell multicollector ICP mass spectrometers (CC-MC-ICP-MS). However, it has been shown that the accuracy of K isotope analysis by CC-MC-ICP-MS could be compromised severely by trace-level Ca contaminants, although the cause of such an effect remains poorly understood. Here, we report that the influence of Ca on K isotope analysis by CC-MC-ICP-MS can be dramatically reduced if D₂ rather than H₂ (the default gas) is used as the reaction gas that goes into the collision cell. This indicates the generation of positively charged calcium-hydride molecules in the collision cell. Usage of D₂ as reaction gas circumvents the Ca-induced inaccuracy issues during K isotope analysis because ⁴⁰CaD⁺ does not interfere with ⁴¹K⁺ as ⁴⁰CaH⁺ does; as such, the robustness of K isotope analysis by CC-MC-ICP-MS is significantly enhanced. This improved method is verified by K isotope analysis of seven geostandards, and applied to China's Chang'e-5 lunar return samples at submicrogram K consumption, revealing significant K isotope variability within a 17 mg lunar basalt fragment.



INTRODUCTION

The element potassium (K) plays an important role in a wide range of chemical, geological, cosmochemical, and biological processes. There has been long interest in using the natural variability of K isotope ratios (i.e., ⁴¹K/³⁹K) of samples to understand the various processes that involve K. For example, Lasnitski and Brewer suggested that ³⁹K is enriched in cancer tissues relative to healthy tissues back in the 1930s and 1940s,^{1–3} although later studies indicated that these early K isotope analyses were not precise enough to reveal the real natural K isotopic variability, which is mostly at the subpermil (<1‰) level.⁴ Researchers continued to use the state-of-the-art mass spectrometry of their times to analyze K isotopes, and the precision of K isotope analysis was improved to ±1‰ in the 1970s by using thermo ionization mass spectrometry (e.g., refs 5 and 6) and to ±0.5‰ in the 1990s by using secondary ionization mass spectrometry (e.g., ref 7), but the precision was still not sufficient to discern most natural K isotope variability from terrestrial samples. Since 2016, multicollector ICP mass spectrometry (MC-ICP-MS) has become the mainstream method to measure ⁴¹K/³⁹K ratios with analytical precision pushed to a level of <0.1‰, which finally opened the door to the full application of stable K isotope ratios to study various natural processes, and an explosion in K isotope research is ongoing.^{4,8–27}

The main challenge in K analysis by MC-ICP-MS is that intense signals of argon hydrides (e.g., ⁴⁰Ar¹H⁺) are generated in ICP, which strongly interfere with K ions (e.g., ⁴¹K⁺) in the mass spectrum. Two approaches have been adopted to overcome this obstacle. One is to run MC-ICP-MS under high mass resolution mode, with cold plasma^{14,15,17,19,23,24,27} or without cold plasma,^{9,11,16} to physically resolve ⁴⁰Ar¹H⁺ from ⁴¹K⁺ in the mass spectrometer. The other approach is to remove ⁴⁰Ar¹H⁺ chemically by collision and reaction with gas molecules in the collision cell of MC-ICP-MS (e.g., refs 8, 10, 13, 18, 20, 25, and 28).

High sensitivity is the main advantage of the collision cell approach over the high mass resolution approach in K isotope analysis by MC-ICP-MS. Sensitivity of 1000–2000 V per μg/g for K can be achieved using a new generation collision cell MC-ICP-MS (CC-MC-ICP-MS),^{8,10,13,18} compared to the typically sensitivity of <30 V per μg/g for K on HR-MC-ICP-MS without a collision cell.^{11,17,19,27} The >1000 V per μg/g

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sensitivity means that, from a counting statistics point of view, precise K isotope ratio measurements can be achieved for a diluted K solution with a concentration as low as 10 ng/g (i.e., 10–20 V total K signal intensity) on CC-MC-ICP-MS. However, the accuracy of K isotope analysis by CC-MC-ICP-MS can be compromised by Ca in the sample solutions, where a $[Ca]/[K]$ of 0.01 can cause a 0.03–0.10‰ offset in measured $^{41}K/^{39}K$ ratios.^{8,10,13,18} Because Ca is a major contaminant that ubiquitously exists in reagents, acids, water, containers, reaction vessels, pipet tips, and air dusts, ng/g to sub-ng/g level background of Ca is common in K analyte solutions, even after careful chemical procedures of purification. Therefore, although sufficient precision of the K isotope ratio measurement is achievable on a 10 ng/g K solution using CC-MC-ICP-MS, the Ca concentration in that 10 ng/g K solution needs to be below 0.1 ng/g (i.e., $[Ca]/[K]<0.01$) to guarantee the accuracy of K isotope analysis. It is extremely challenging, if not impossible, to keep the Ca concentration in solutions at a sub-ng/g to pg/g level routinely for a regular isotope laboratory. To date, most CC-MC-ICP-MS laboratories run K isotope analysis on solutions that contain 150–250 ng/g K.^{8,10,13,18}

In order to take full advantage of the high sensitivity of CC-MC-ICP-MS and increase the robustness of CC-MC-ICP-MS for K isotope analysis on precious and small samples (e.g., extraterrestrial specimens), it is important to address the inaccuracy induced by Ca during K isotope analysis. In this report, we show that when D₂ rather than H₂ is used as the collision gas, the susceptibility of measured $^{41}K/^{39}K$ ratios to Ca is reduced to a negligible level; thus, the robustness of K isotope analysis by CC-MC-ICP-MS is greatly enhanced. The improved mass spectrometry (D₂ as collision gas) was successfully applied to K isotope analysis of the returned lunar samples by China's Chang'e-5 mission.

MATERIALS AND METHODS

In December 2020, four decades after the United States' Apollo missions and the USSR's Luna missions, China's Chang'e-5 (CE-5) mission returned 1.731 kg of lunar soil from the Oceanus Procellarum region of the Moon. Only a very small fraction of the returned samples was distributed to institutes in China for research purposes. In this study, the authors were granted a tiny lunar basalt rock fragment (sample no. CE5C0000YJYX048) from the Chang'e-5 return mission's lunar sample for destructive K isotope analyses. The 17.6 mg rock fragment was gently crushed between two glass slides to be broken into mineral grains, which were separated using tweezers under a binocular microscope (see Figure S1 and related text, Supporting Information). Mineral separates of plagioclase and pyroxene were picked up for K isotope analysis. Each sample aliquot consisted of four to six mineral grains that weighed 100–300 μg in total. In addition, six international rock standards from the United States Geological Survey (USGS) and one Hawaii seawater sample were processed and analyzed to assess the accuracy and reproducibility of the whole chemical and analytical procedure. The rock standards were selected to represent a wide spectrum of rock matrix, including basalts (BCR-2, BHVO2), dolerite (DNC-1a), andesite (AGV-2), granodiorite (GSP-2), and an organic-rich sedimentary rock standard of oil shale (SGR-1). The K isotope compositions of these standards have been reported by other laboratories, which allows interlaboratory comparisons.

The samples were digested in mixed HF-HNO₃ acids in tightly capped Teflon beakers and then treated by a well-established two-stage ion-exchange column procedure²⁵ to separate K from other matrix elements. Recovery of K was >99.0%, and the total procedural blank was 3.6–7.8 ng ($n = 10$, done along with lunar samples).

Isotopic analysis of K was performed on a Nu 1700 Sapphire MC-ICP-MS instrument housed at Nanjing University. The instrument is equipped with a double-path collision cell^{8,10,13,18} to allow operation in two different modes, which are the “low-energy” mode that involves the collision cell, and the conventional “high-energy” mode. The method in this study is established in the “low-energy” (collision cell) mode with H₂ or D₂ as the reaction gas and He as the collision gas. The settings of the instrument are summarized in Table 1. The sensitivity of the instrument for K was 600–1000 V per μg/g. The on-peak background of ^{39}K was 0.8–1.5 V, equivalent to 1–2 ng/g of K.

Table 1. Instrument Parameters of the Mass Spectrometer and Desolvator for K Isotopes Measurements in This Study

Mass Spectrometer: Nu 1700 Sapphire MC-ICP-MS	
RF power	1300 W
cooling gas	13.0 L/min
auxiliary gas	1 L/min
nebulizer gas	~30 psi
source slit	fully open
α slit	half open
resolving power	4500
acceleration	~4000 V
extraction	~2360 V
Q1	30.3
Q2	−23.5
hexapole RF ref.	1.5
RF bias ref.	0
cell gas He flow rate	3 sccm
cell gas H ₂ /D ₂ flow rate	5 sccm
Desolvator: Aridus3	
spray chamber temperature	110 °C
desolvator temperature	140 °C
Aridus Ar sweep gas flow	~6.0 L/min
N ₂ flow	0 mL/min
Data Acquisition	
uptake rate	~120 μL/min
transfer time	50 s
integration time	5 s
number cycles	40
cup configuration	H6 (^{42}Ca , $10^{11} \Omega$), H1 (^{41}K , $10^{11} \Omega$), D0 (^{40}Ar), L5 (^{39}K , $10^{10} \Omega$)

Mass bias and instrumental drift during K isotope analysis were corrected using a standard–sample–standard bracketing routine. Typically sample and standard solutions were diluted to 250 ± 5 ng/g for isotope analysis, except for analyses of lunar samples and companion standards when the solutions were all diluted to 100 ± 2 ng/g. Each isotopic analysis consisted of 40 cycles of 5 s integration time. This routine results in a typical internal precision (2 relative standard error) of $^{41}K/^{39}K$ ratio better than $\pm 0.04\%$. Potassium isotope data

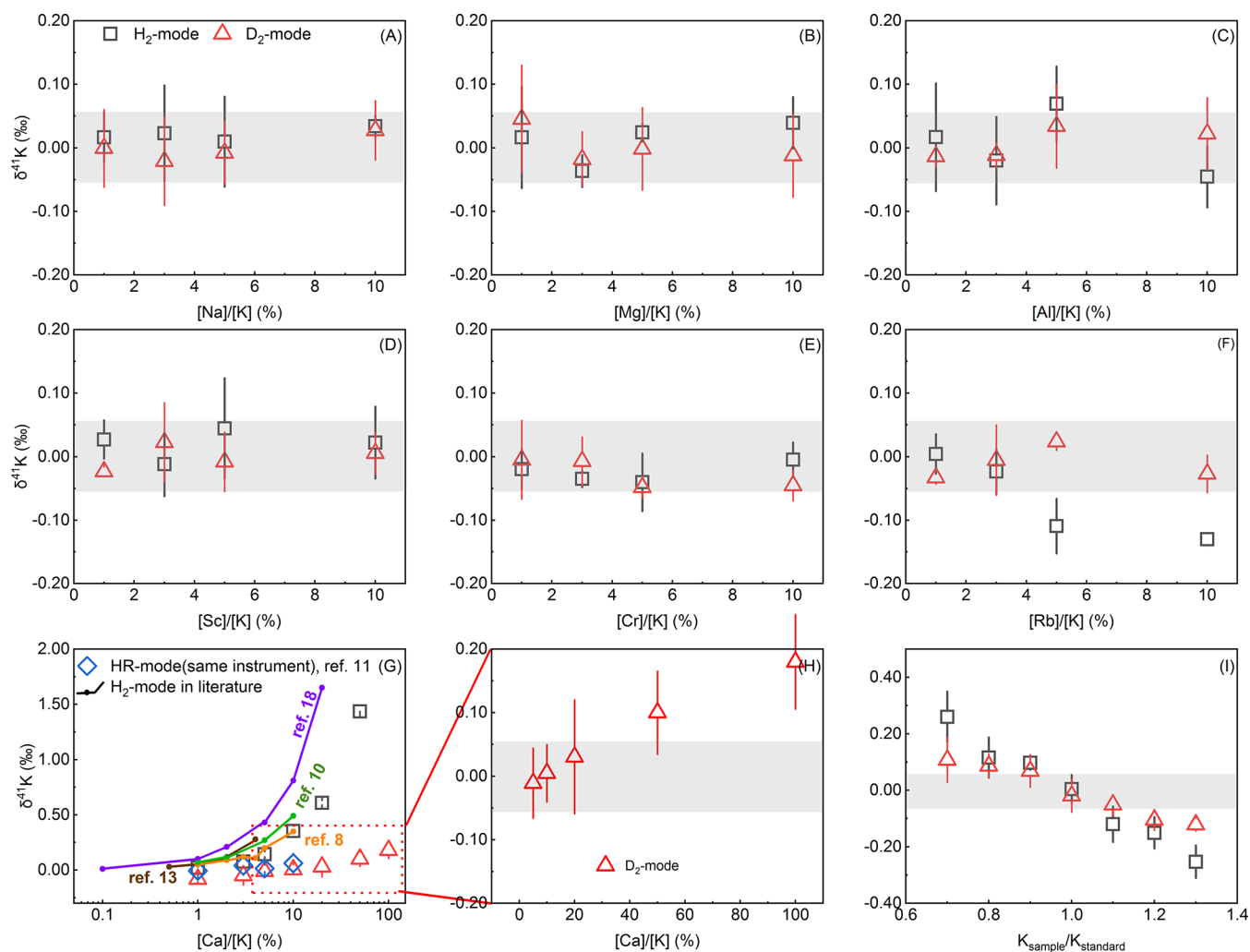


Figure 1. Effect of the matrix elements (A–H) and standard-sample concentration mismatch on K isotope measurements (I). Plots A–H show the measured isotope data for K solution doped with different matrix elements against the same K solution. In plot I, both sample and standard solutions contained the same K, but the K concentration of the sample solution varied. The shaded areas denote an external analytical precision ($\pm 0.06\text{‰}$) of the method. Error bars denote 2SD of multiple analyses. Literature data for Ca-induced inaccuracy are from refs 8, 10, 13, and 18.

are reported in $\delta^{41}\text{K}$ for $^{41}\text{K}/^{39}\text{K}$ ratios, following the IUPAC guideline:²⁹

$$\delta^{41}\text{K} = \left[\left(\frac{^{41}\text{K}/^{39}\text{K}_{\text{sample}}}{^{41}\text{K}/^{39}\text{K}_{\text{standard}}} \right) - 1 \right] \quad (1)$$

where the $\delta^{41}\text{K}$ values are expressed in permil (‰) notation (i.e., results of eq 1 times 1000 in number). For geologic and lunar samples, the reference standard was NIST SRM 3141a;^{4,25} thus, the data are reported in $\delta^{41}\text{K}_{\text{NIST3141a}}$.

Prior to analyses of lunar and geological samples, a series of tests were undertaken to evaluate the performance of the mass spectrometer under different conditions. These tests included cation-doping tests and a K intensity mismatch test. For the cation-doping test, different cations were added to an in-house K standard solution to make a series of solutions with $[\text{matrix}]/[\text{K}] = 1\%$, 3% , 5% , and 10% , which were measured against the pure K standard. For the K intensity mismatch test, a set of in-house K standard solutions of variable concentrations (e.g., 175–325 ng/g) were analyzed as samples against the standard solution with a fixed K concentration (e.g., 250 ng/g) intensity mismatch on K isotope ratio analysis.

RESULTS AND DISCUSSION

Matrix Effects. For K isotope analysis by MC-ICP-MS, inaccuracy can be caused by the existence of matrix elements in K sample solutions and the mismatch in K concentration between sample and standard solutions.^{13,15,18,19,27} The response of CC-MC-ICP-MS with H₂ or D₂ as the reaction gas to different matrix effects was tested, and the results are shown in Figure 1. For five matrix elements (Na, Mg, Al, Sc, Cr), the measured $\delta^{41}\text{K}$ values remain accurate (i.e., within $\pm 0.06\text{‰}$) when the $[\text{matrix}]/[\text{K}]$ ratio is within 10% regardless of H₂ or D₂ being used as the reaction gas for CC-MC-ICP-MS (Figure 1A–E). However, when [Rb]/[K] ratio is greater than 5%, the $\delta^{41}\text{K}$ measured by CC-MC-ICP-MS with reaction gas of H₂ is significantly offset by $>0.1\text{‰}$; by contrast, when D₂ is used as the reaction gas for CC-MC-ICP-MS, the $\delta^{41}\text{K}$ values remain accurate even when [Rb]/[K] reaches 10% (Figure 1F). Note that the cation-doping test for Rb had been repeated in different analytical sessions, and the phenomenon of Figure 1F was reproducible (additional results are given in Figure S2).

The most remarkable contrast in instrument behaviors between the H₂-mode (i.e., when H₂ was used as the reaction

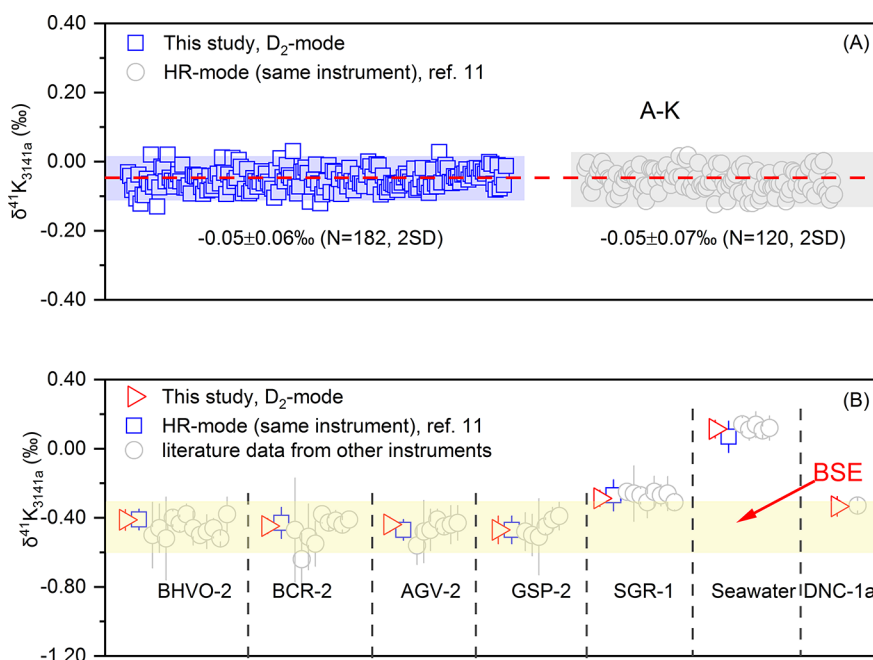


Figure 2. (A) Compilation of $\delta^{41}\text{K}$ for in-house pure K standard A-K measured against NIST SRM 3141a in this study and that in An et al. (2022), ref 11. (B) Comparison of the $\delta^{41}\text{K}$ data of different geostandards measured in this study (red \triangleright) to those measured on a Nu 1700 Sapphire instrument in a high-energy path (blue \square) and to those reported by other laboratories (gray \circ). All data in this figure are normalized to NIST SRM 3141a with 2SD error bars.

gas for the collision cell) and the D₂-mode was found for cation-doping tests of Ca (Figure 1G,H). When H₂ is used as the reaction gas of the CC-MC-ICP-MS, the measured $\delta^{41}\text{K}$ is highly susceptible to Ca in the K solution, and when $[\text{Ca}]/[\text{K}]$ is 5%, the measured $\delta^{41}\text{K}$ values are inaccurate by 0.15‰ (Table S1 and Figure 1G). Such phenomena have been reported in all recent studies of the K isotope method developed using CC-MC-ICP-MS.^{8,10,13,18} However, when D₂ is used as the reaction gas of the CC-MC-ICP-MS, Ca no longer causes significant inaccuracy to measured $\delta^{41}\text{K}$ values, so even when $[\text{Ca}]/[\text{K}]$ was 1:1, the deviation of the measured $\delta^{41}\text{K}$ value was within 0.20‰ (Table S1 and Figure 1H). This contrast can be explained by generation of calcium-hydride in the collision cell, where when H₂ is used as the reaction gas, $^{40}\text{CaH}^+$ is generated and interferes with $^{41}\text{K}^+$, causing analytical artifacts of elevated measured $\delta^{41}\text{K}$ values; by contrast, when D₂ is used as the reaction gas, $^{40}\text{CaD}^+$ is generated, and with a mass number of 42, it does not interfere with $^{41}\text{K}^+$. Based on the measured K isotope data, and assuming both Ca and K are quantitatively ionized in ICP, we estimate that the generation rate of singly charged calcium-hydride from $^{40}\text{Ca}^+$ is on the order of $\sim 7 \times 10^{-4}$ in the collision cell.

A negative correlation between measured $\delta^{41}\text{K}$ and K intensity mismatch is observed in both the H₂-mode and D₂-mode of the CC-MC-ICP-MS (Table S2 and Figure 1I). However, the slope is less steep for D₂-mode, suggesting that when D₂ is used for the collision gas, the instrument is less sensitive to the mismatch of K concentration between sample and standards. Such a test of the K intensity mismatch effect had been repeated under different circumstances, and the reduced sensitivity to concentration mismatch in D₂-mode compared to H₂-mode was found to be reproducible (an additional example is given in Figure S6). Synthesizing the tests above, we conclude that K isotope analysis by CC-MC-ICP-MS is more robust to matrix effects in the D₂-mode than

in the H₂-mode, and the improvement is the most significant for the contaminant of Ca.

Precision and Accuracy. Repeat analyses of in-house K standard solution against the NIST SRM 3141a standard over six months yielded a long-term external reproducibility (2σ) of $\pm 0.06\text{‰}$ for D₂-mode of the CC-MC-ICP-MS (see Table S3 and Figure 2A). This is slightly better than the long-term external reproducibility of K isotope analysis using the high-resolution mode on the same instrument (Figure 2A). Based on systematic analyses of standard solutions of variable K concentrations, the analytical uncertainty of K isotope ratios was mainly contributed from short-time-scale instrument instability and instrumental on-peak background (Figures S3 and S4). For K solutions with concentration below 30 ng/g, the on-peak background contributed more than 50% of the analytical error of the measured K isotope ratios, and the internal precision deteriorated remarkably (i.e., 2 standard relative error $> 0.04\text{‰}$; Figure S4).

The K isotope compositions of seven common geostandards have been measured by CC-MC-ICP-MS under the D₂-mode. The $\delta^{41}\text{K}$ values for DNC-1 ($-0.33 \pm 0.06\text{‰}$, 2SD, $N = 10$), AGV-2 ($-0.44 \pm 0.04\text{‰}$, $N = 12$), GSP-2 ($-0.47 \pm 0.08\text{‰}$, 2SD, $N = 16$), SGR-1b ($-0.29 \pm 0.05\text{‰}$, 2SD, $N = 13$), BHVO-2 ($-0.41 \pm 0.06\text{‰}$, 2SD, $N = 12$), BCR-2 ($-0.45 \pm 0.04\text{‰}$, 2SD, $N = 14$), and seawater ($+0.11 \pm 0.05\text{‰}$, 2SD, $N = 14$) all agree well with previously published data (see Table S4 and Figure 2B). Additionally, tests show that precise and accurate K isotope analyses are attainable with a solution K concentration as low as 30 ng/g (details are given in the Supporting Information and Figure S5). These results attest to the validity of the method developed in this study, which is applicable to low-K and high-Ca samples.

Application to the Lunar Sample Returned by the Chang'e-5 Project. The K isotope ratios of the six mineral-separated samples were measured using the CC-MC-ICP-MS

under D₂-mode. The mass of K in the mineral-separated samples ranged between 420 and 820 ng (Table S5), and the sample solutions were diluted to 100 ng/g for K isotope analysis. Note that seawater and rock standards with K masses down to 300 ng were also processed and measured at a solution concentration of 100 ng/g, and the results validate the analytical accuracy (Table S5). The three feldspar mineral separate samples from the lunar basalt fragment show a large variation in $\delta^{41}\text{K}$ values, ranging from -0.60‰ to $+0.03\text{‰}$; by contrast, the three pyroxene mineral separate samples show a tight distribution of $\delta^{41}\text{K}$ values, between -0.37‰ and -0.18‰ (Table S5 and Figure 3A). These values are

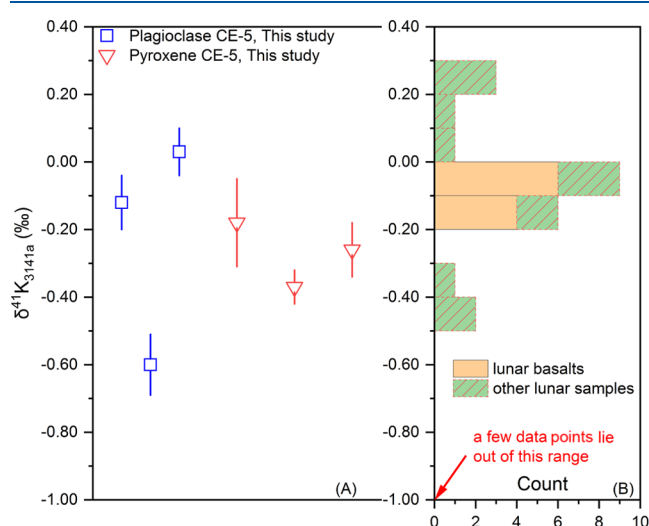


Figure 3. (A) K isotope compositions of plagioclase and pyroxene mineral-separated samples from the returned lunar samples of China's Chang'e-5 mission. (2) K isotope compositions of bulk lunar rocks in previous studies.³⁰

comparable with the reported K isotope compositions of bulk lunar rocks (e.g., ref 30; Figure 3B). This is the first time that significant K isotope heterogeneity has been revealed for lunar basalt at the mm scale, and the K isotope heterogeneity likely was caused by kinetic K isotope fractionation during feldspar crystallization, which occurred at the late stage of lunar basalt magmatism.

CONCLUSIONS

In this study, we report that the robustness of K isotope analysis using CC-MC-ICP-MS can be improved using D₂ as the reaction gas instead of H₂. In particular, the analytical inaccuracy caused by Ca in the K solution is dramatically reduced in D₂-mode of CC-MC-ICP-MS. This shows the generation of positively charged calcium hydride in the collision cell of ICP mass spectrometers, with a generation rate of $\sim 7 \times 10^{-4}$ calcium hydride per ionized Ca⁺. The accuracy and precision of K isotope analysis under the D₂-mode of CC-MC-ICP-MS are validated by systematic analyses of different international geological standards. The improved method was applied to the lunar samples returned by China's Chang'e-5 project and yielded precise K isotope data for mineral separate samples that weigh only 0.1–0.3 mg, with submicrogram K consumption. The measured $\delta^{41}\text{K}$ values of the mineral-separated samples vary between -0.60‰ and $+0.03\text{‰}$, for the first time revealing significant K isotope

fractionation at millimeter-scale during lunar magmatic activities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.2c03989>.

Additional experimental details, description of sample materials, data set, and results of some repeated experiments (PDF)

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Notes

The authors declare no competing financial interest.

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