Potassium isotopic composition of various samples using a dual-path collision cell-capable multiple-collector inductively coupled plasma mass spectrometer, Nu Instruments Sapphire

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Abstract:

Mass-dependent K isotopic fractionations can be used to trace cosmochemical, geological, and biological processes such as evaporation/condensation, core formation, magmatic processes, weathering, and cellular metabolism. However, the application of stable K isotopes has been limited by major isobaric interferences from Ar, common on conventional multi-collector inductively-coupled-plasma mass-spectrometer (MC-ICP-MS), particularly for the low-K samples. Here, we present a set of high-precision K isotopic data acquired on terrestrial rocks, seawater, as well as a lunar meteorite using the recently released Nu Sapphire™ MC-ICP-MS that utilizes a collision cell to minimize Ar based interferences while maintaining remarkably high K sensitivity (≈ 2000V/ppm). The influence of several parameters on the precision and accuracy of the K isotopic data has been evaluated, including total K concentration, K intensity mismatch between sample

and standard, HNO_3 molarity mismatch between sample and standard, and the presence of matrix elements. We found that the Nu Sapphire™ can be used to acquire precise and accurate data using as little as 125ng of K, which represents an improvement by a factor 10 compared to what has been done on previous instruments. We present data for 23 previously analyzed samples; these data are highly consistent with literature values. On the other hand, accurate measurements are conditioned 1) to the close matching of sample and standard K intensities (a 1% mismatch creates a 0.02 ‰ offset on the $^{41}K/^{39}K$ ratio), and 2) to the absence of Ca (a Ca/K ratio of 1% creates a 0.069 ‰ offset on the $^{41}K/^{39}K$ ratio). In addition, Rb/K, Na/K, Ti/K and Cr/K ratio should also be maintained under 2.5% to avoid isotopic offset.

We confirm the existence of significant mass-dependent K isotopic variations in terrestrial samples and that lunar rocks are isotopically heavier than terrestrial rocks. The incomparable sensitivity offered by the Nu Sapphire opens the possibility for high-precision K isotopic measurements across a wide range of samples for diverse applications.

Introduction

Potassium is a major or an important minor element in most geological and biological environments. Potassium is the 20th most abundant element in the Sun, and the 17th on Earth (Palme et al., 2014). Due to its incompatible behavior during magmatic processes, K is highly enriched in the continental crust, which is a major terrestrial reservoir that contains ≈24% of the total K (Rudnick and Gao, 2003). It is also a highly water-soluble element and a major cation in seawater (Bruland and Lohan, 2003). In biological systems, K is fundamental in cell biochemical reactions, energy metabolism, and is essential to cellular osmotic regulation and the propagation of the nerve impulses through cell membranes (e.g. Carver, 2019). It is inferred to be one of the light elements in the terrestrial (Gessmann and Wood, 2002) and lunar (Steenstra et al., 2018) cores due to its siderophile behavior under high-pressure conditions. Moreover, K is a moderately volatile lithophile element (temperature of 50 % condensation = 1006 K, Lodders, 2003), with an abundance that varies greatly between planetary bodies and understanding the origin of these variations may hold clues to the mechanisms of planetary formation (e.g. Humayun and Clayton, 1995).

Potassium has 2 stable isotopes: ^{39}K (93.258 %) and ^{41}K (6.730 %) and a long-lived radioactive isotope (^{40}K, $T_{1/2}$=1.248×10^9 years, 0.0117 %). In this work, the isotope composition of K refers to the mass-dependent fractionation of stable isotopes ^{39}K and ^{41}K. The difference in the ratio of ^{41}K/^{39}K can be used to decipher the different processes governing the origin of its abundance variations (e.g. evaporation/condensation, core formation, magmatic processes, weathering, disease affecting it imbalance in the organism). For example, Wang and Jacobsen (2016) found that the Moon is isotopically

heavier in K isotopes compared to the Earth, and suggested that this reflected volatile events during Moon formation.

While potassium is one of the elements with the lowest first ionization potential, ≈4.34 eV (https://physics.nist.gov/PhysRefData/ASD/ionEnergy.html), there have been relatively limited high precision isotopic studies because of major drawbacks on both multi-collector thermo-ionization (TIMS) and inductively-coupled plasma (MC-ICP-MS) mass spectrometers and in-situ measurements by secondary ion mass spectrometers (SIMS) returned precision of ≈ 0.5 ‰ (Humayun and Clayton 1995). Because K has only 3 natural occurring isotopes, it is not possible to correct for instrumental mass bias by double spike addition which therefore limits the precision that can be obtained for stable isotope ratios by TIMS to ≈1 ‰ at best (e.g. Verbeek and Schreiner, 1967). On the other hand, MC-ICP-MS has become the instrument of choice to analyze elements with 2 or 3 stable isotopes mostly because of its rapid sample throughput and compatibility with sample-standard bracketing method for mass bias correction (e.g. Lu, (Blichert-Toft et al., 1997), Cu (Maréchal et al., 1999)). However, ionization is obtained in an Ar plasma for conventional MC-ICP-MS, which generates major isobaric interferences as $^{38}ArH^+$, $^{40}Ar^+$ and $^{40}ArH^+$ on ^{39}K, ^{40}K and ^{41}K, respectively, which makes high-precision K isotopic measurements more cumbersome than for most elements. One approach to circumvent these problems has been to limit argides generation at a decreased Ar plasma temperature and to resolve the interferences at an increased mass resolution (e.g. Chen et al., 2019 ; Hu et al., 2018; Morgan et al., 2018; Tuller-Ross et al., 2019; Xu et al., 2019). Using this technique, $^{41}K/^{39}K$ reproducibility as precise as ≈50 ppm (2SE) can be obtained but it necessitates the use of over 5 μg of K (Chen et al., 2019; Hu et al., 2018 ;

Xu et al., 2019). Recently Chen et al. (2020) also achieved a similar precision with a dry plasma method where an Apex Omega desolvating nebulizer system was used to suppress the formation of argon hydrides without lowering the RF power. Alternatively, collision cell MC-ICP-MS, theoretically allows the reduction of the amount of charged argides via collision and reaction with a neutral or reactive gas. Until recently (Ku and Jacobsen, 2020), only the Micromass Isoprobe, which is an older generation single-focusing MC-ICP-MS had been equipped with such collision cell. For example, Li et al. (2016) performed isotopic measurements on a Micromass Isoprobe using D_2 as the collision gas, and obtained a precision of ≈200 ppm (2SD) for $^{41}K/^{39}K$ with a couple of μg of K samples being analyzed. A new generation of dual-path MC-ICP-MS with collision cell capability has been released by Nu Instruments in 2018, known as the Sapphire. It is promising to obtain high-precision K isotopic data on small samples with this novel instrument because it is the first MC-ICP-MS to combine stat-of-the-art interface, double-focusing ion optics, and a collision cell, to allow testing the accuracy of the data obtained using pseudo-high resolution and the older generation collision cell instrument. So far only one paper reported K isotopic data measured on this instrument (Ku and Jacobsen, 2020); their analyses use ≈1 μg of K and yield an internal precision (2SE) of 30 ppm and an external reproducibility (2SD) of 27 ppm over a 9-day period. However, this paper focused on the potassium isotopic composition of meteorites and report only 5 data for terrestrial rock geostandards (including seawater). Here we report new data obtained on 23 samples, including a large variety of international geostandards on which data had been previously acquired by pseudo-high resolution on a Neptune Plus or on a Nu Plasma II. Furthermore, we report the limitation on the accuracy of the data obtained from

various analytical effects such as the effect of Ca (that would produce CaH^+ interference on ^{41}K) and on the intensity mismatch between samples and standard.

Samples and Methods

Samples

The samples analyzed here comprise W-1 (diabase, United States Geological Survey, USGS), JB-1 (basalt, Geological society of Japan, GSJ), SGR-1 (shale, USGS), GSP-1 (granodiorite, USGS), AGV-1 and AGV-2 (andesite, USGS), BHVO-2 (basalt, USGS), BCR-2 (basalt, USGS), G-2 (granite, USGS), SY-1 and SY-2 (Syenite, Canadian Certified Reference Materials Project, CCRMP), MAG-1 (marine mud, USGS), Hawaiian seawater (internal standard, University of Washington), GH (granite, Centre de Recherches Pétrographiques et Géochimiques, CRPG), GA (granite, CRPG), GBW07111 (granite, National Research Center for Geoanalyses of China, NRCG), GBW07103 (granite, NRCG), FK-N (Feldspar potassium, ANRT), SDC-1 (Mica shist, USGS), QLO-1 (quartz latite, USGS), DRN (diorite, ANRT), RGM-1 (rhyolite, USGS) and LAP 02224 (lunar meteorite). The Hawaiian seawater is an internal standard from the University of Washington, but as demonstrated before (Hill et al. 2019, Wang et al. 2020), seawater is homogeneous regardless of location, depth, or K concentration, and therefore it can be taken as representative of global seawater. The selected samples cover a range of chemical compositions and most of them have previously been analyzed for their K isotopic compositions in multiple laboratories. Therefore, they are well suited to test the accuracy of the Nu Sapphire measurements, as well as to confirm previous results obtained on standard MC-ICP-MS. Furthermore, BHVO-2 has been used to evaluate the

long-term reproducibility of the method and has been analyzed 11 times over a 6-month period from three separate dissolutions and chemical purifications (Table S1).

To evaluate the effect of the intensity mismatch between sample and standard we performed tests on a pure K concentration standard (NIST SRM 3141a) as well as on one geological material (DR-N) running them both with 0 to 10 % intensity mismatch, as compared to the bracketing standard (NIST SRM3141a). The effect of $^{40}CaH^{+}$ interference on ^{41}K has also been tested on both the pure K standard and on one geological material (GH) by adding Ca up to 4%. Finally, we tested the effect of K concentration on the accuracy of the data from 150 ppb down to 25 ppb of K (which for 5 replicates would represent ≈750 and ≈125 ng of K, respectively).

Dissolution and chemical purification

The chemical purification has been conducted at either the Institut de Physique du Globe de Paris (IPGP), and University of Washington as described here (Xu et al., 2019) or at Washington University in St Louis as described in Chen et al. (2019). At Washington University, all samples were grounded in an agate mortar. 50-100 mg of powders were dissolved in concentrated HF-HNO_3 following by a second dissolution in HCl-HNO_3 using Parr sample digestion vessels for both steps. Then samples were dried down and re-dissolved in 0.7 N HNO_3. Potassium is purified using a two-step ion exchange chromatography. The first separation is done on a “big” column (Bio-Rad Econo-Pac; I.D.=1.5cm) filled with 17 mL of AG50-X8 100–200 mesh cation-exchange resin. A second purification is done on a “small” column (Bio-Rad glass Econo-column; I.D.=0.5cm) filled with 2.4 mL of the same resin. Both columns were first cleaned with 6

N HCl. Samples in 1 mL of 0.7 N HNO_3 were loaded on the "big" columns. First 87 mL of 0.7 N of HNO_3 are passed to clean up the matrix. The K fractions were collected by adding 107 mL of 0.7 N HNO_3. On the second column, the samples are loaded in 1 mL of 0.5 N HNO_3. Matrix were eluted using 16 mL 0.5 N HNO_3. 18 mL of 0.5 N HNO_3 are then added to collect the K.

At IPGP and University of Washington, 20-25 mg pulverized rock standards were digested sequentially using Optima-grade concentrated HF-HNO_3, HCl-HNO_3, and HNO_3. The closed beakers were heated on a hotplate at 120°C, periodically vibrated in an ultrasonic bath, and opened and dried at 100°C. The dried samples were redissolved in 0.5 N HNO_3 in preparation for the cation-exchange chromatography. Potassium was purified by two passes of 2mL pre-cleaned Bio-Rad AG50W-X8 resin (200-400 mesh) that was filled in Bio-Rad Poly-Prep polyethylene columns and conditioned by 10 mL 0.5 N HNO_3. Sample solutions were then loaded on the resin and eluted by 0.5 N HNO_3. Matrix elements were eluted with 13 mL of 0.5 N HNO_3, and K was collected from the subsequent 22 mL fraction. The resin was cleaned with 10 mL of 6 N HCl afterward.

To minimize procedure blank, acid-washed teflon beakers and double-distilled acids were used exclusively in this study, which were prepared in house at either Washington University in St Louis, University of Washington, USA, or at IPGP.

K isotopic measurements on Sapphire

Collision cells have been in use with quadrupole ICP-MS for nearly 20 years and have proven effective to remove Ar based species and other molecular interferences. But it is also known to create complications for isotope systems due to the mass discrimination effects of the multipole and inherent instrumental isotopic bias.

The Nu Sapphire features by a dual-path design (Figure 1), including both a conventional MC-ICP-MS (High Energy, 6 kv acceleration) pathway and a collision cell (Low Energy, 4 kv acceleration) pathway. This design allows for selecting either classic or novel applications without compromising the analysis. For K isotope measurements, we used the collision cell pathway.

The Nu Sapphire installed at IPGP is a double-focusing magnetic sector MC-ICP-MS instrument equipped with 16 fixed Faraday collectors that are fitted with selectable resistors ranging from 10^{10} to 10^{13} ohm. For the low energy pathway, at the plasma source, the ions are accelerated at 4kV. The ions are deflected off-axis and decelerated to a few 10eV's of energy to enter the radio frequency (RF) multipole collision/reaction cell. The RF hexapole reduces mass bias effects compared to quadrupole-based cells due to the larger mass transmission window. This is because quadrupoles have the steepest confining potential, i.e., the potential rises quickly from the center of the device to the rods, thus permitting operation within a narrow bandwidth as well as operation in other modes that are highly selective with respect to the mass-to-charge ratio (Amr, 2012). Hexapoles, on the contrary, are much less selective with respect to the mass-to-charge ratio, but can provide higher ion transmission and reduced scattering losses.

Within the gas filled cell the ions are collisionally thermalized by colliding with the buffer background gas, and charge exchange takes place with hydrogen, removing the Ar based species. After the cell, the ions are re-accelerated to 4 kV and focused back onto the mass spectrometer source slit in the same manner as on a conventional MC-ICP-MS (or as if it were following the high energy path on the Nu Sapphire).

The charge exchange with H_2 gas in the collision/reaction cell reduces the Ar^+ signal by greater than 9 orders of magnitude, to almost completely remove any Ar based species, for example:

$Ar^+ + H_2 \rightarrow Ar + H_2^+$ Eq. 1

$ArH^+ + H_2 \rightarrow ArH + H_2^+$ Eq. 2

In addition to the hydrogen gas required for the reaction, He gas is introduced in the cell as a buffer gas and contributes to the collisional thermalisation of the ions within the cell in order to maximise transmission through the hexapole ion guide. The relative amount of He and H_2 introduced in the cell is optimised to minimise the Ar^+, ArH^+ and CaH^+ backgrounds (see Table 1 for the parameters used here).

In this study, the K isotope data were acquired on the Sapphire instrument in its Low Energy mode. A 150 ng/g (ppb) NIST SRM3141a K standard solution and various samples were introduced into the mass spectrometer using an Apex Omega desolvating system fitted with a 100 µL/min PFA nebulizer (MicroFlow nebuliser, Elemental Scientific, Omaha, NE, USA) and with standard Ni dry cones ("dry plasma"). We also performed comparative test using a cyclonic spray chamber ("wet plasma"). Zoom optics were used to optimize focusing and peak coincidence.

Data was collected in static mode (no peak jump), with $^{39}K^+$ measured in a Faraday cup (L5) connected to a pre-amplifier fitted with a 10^{10}ohm resistor and $^{41}K^+$ using a 10^{11}ohm resistor (L1). The intensity of the mass 40 was monitored on the faraday cup L3 using a 10^{11} ohm resistor. Each analysis consists of a 60-second zero measurement in 3% HNO_3, followed by 1 block of 50 cycles with 5 second integrations

(Table 1). A 90-120 second wash was performed in 3 % HNO_3 between each standard and sample analysis and a transfer time of 60 or 90 seconds was applied. Each sample was measured between 6 and 12 times, bracketed by the NIST-SRM 3141a standard. No tuning was made once the sequence had begun. The operating parameters of the instrument are listed in Table 1.

In these conditions, the background on the masses 39 and 41 were approximatively 150 mV and 2 V respectively in dry plasma mode and 39 mV and 450 mV in wet plasma mode. The signal on the mass 40 were approximatively between 20 and 100 mV in dry plasma mode and 24 and 62 mV in wet plasma mode. For comparison, the signal for 150 ppb of K returned over 300 V in dry plasma mode and 20 V in wet plasma mode.

All the samples and tests have been performed in dry plasma mode. The wet plasma mode has only been run to compare the precision and intensity of the SRM3141a K standard solution to previous studies (Chen et al., 2019; Li et al., 2016; Li et al., 2020; Morgan et al., 2018; Xu et al., 2019). The mass bias was corrected by measuring the samples alternatively with the NIST SRM3141a K standard solution (standard-sample bracketing).

Results and discussion

The K isotopic data for the samples are reported in Table 2. All the data for the analytical tests and long-term reproducibility are reported in supplementary tables.

All the data are reported using the $\delta^{41}K$ notation as:

$$\delta^{41}\mathrm{K}\ (‰) = \left[\frac{\left(\frac{^{41}\mathrm{K}}{^{39}\mathrm{K}}\right)_{\mathrm{sample}}}{\left(\frac{^{41}\mathrm{K}}{^{39}\mathrm{K}}\right)_{\mathrm{SRM3141a}}} - 1\right] \times 1000 \qquad (3)$$

The errors are reported as the 2 standard-deviation of the replicated measurements as well as the 95% confidence interval (see Hu et al. 2018 for details).

Accuracy and long-term reproducibility

The accuracy of our analytical protocol is confirmed by 1) self-bracketing pure K standards that had expected δ^{41}K of zero (Fig. 2), 2) measuring 19 well-characterized geostandards that were previously analyzed at UW (Table 2) and replicating the chemical purification of FK-N geostandard and the seawater at IPGP. The δ^{41}K values of these geostandards obtained on the Nu Sapphire at IPGP are consistent with those measured on a Nu Plasma II at UW (Table 2). We also fully processed BHVO-2, BCR-2, and AGV-2 at IPGP; their δ^{41}K values agree well literature data (Table 2).

The long-term reproducibility of the K isotopic measurement was evaluated by repeated measurements of BHVO-2 during 11 analytical sessions (where in each session BHVO-2 was analyzed between 6 and 10 times) over 6 months, on three separate dissolution and chemical purification (see Table S1). We obtained an average δ^{41}K of -0.434±0.040 ‰ (2SD, n=11), which is consistent with literature values (δ^{41}K= -0.411±0.012 ‰, Xu et al. 2020). Our results reveal a long-term reproducibility of 0.040 ‰ (2SD).

Comparison of Sapphire with previous methods

Figure 2 illustrates the sensitivity of the double-focusing, dual-path collision cell-capable Sapphire instrument for K isotopic measurement compared to previous methods

using either older generation, single-focusing collision cell MC-ICPMS (Li et al., 2016) or no collision cell, double-focusing MC-ICPMS in high energy and cold or hot plasma (Chen et al., 2019 ; Hu et al., 2018; Morgan et al., 2018; Tuller-Ross et al., 2019; Xu et al., 2019). The sensitivity is reported to reflect a standard at 150 ppb K for each method. The Sapphire provides the highest reproducibility both in wet and dry plasma mode compared to any previous method, as well as the highest sensitivity even when only using the wet plasma compared to high resolution/dry plasma on conventional MC-ICP-MS. Given the gain in sensitivity by over a factor of 30 when coupled to the Apex Omega we have decided to perform most of the tests presented below, as well as the measurement of the natural samples, in these conditions.

Effect of K concentration on accuracy

While all the samples have been analyzed using 150 ppb K (≈750 ng of K for 5 replicates), we have performed tests to evaluate the accuracy of the measurements down to 25 ppb K (≈125 ng of K for 5 replicates) (Figure 3). For both the pure K standard (Figure 3a) and for a rock sample (DR-N, Figure 3b), the accuracy is maintained down to 25 ppb K. For DR-N the value obtained when running 25ppb of K ($\delta^{41}K$ = -0.555±0.028 ‰) is consistent with the value obtained at 150 ppb ($\delta^{41}K$ = -0.566±0.034 ‰) as well as with literature data (shown as the grey bar on Figure 3b, $\delta^{41}K$ = -0.562±0.025 ‰, (Xu et al., 2019)). This method is therefore very promising for analyzing samples with low K content. For example, the solution at 25 ppb of K of DR-N was run 8 times (i.e. 200 ng of K) for a precision of 0.028 ‰ and analyzing it only 5 times (125 ng of K) would provide similar precision. This is a major gain compared to previous methods that would require several micrograms of K for similar quality of data.

Effect of K concentration mismatch

The effect of intensity mismatch tests was tested by maintaining the NIST-SRM 3141a bracketing standard at 150 ppb of K while varying the concentration of both the NIST-SRM 3141a K standard measured as a sample (Figure 4a) or the rock sample (granite GA) from 10 % lower to 10 % higher concentrations. In Figure 4, the variation of $\delta^{41}K$ values is plotted as a function of the ratio between the K concentration of the sample analyzed (at various concentrations) and of NIST-SRM 3141a analyzed at 150 ppb. Both the pure K standard and granite GA sample show consistent correlation between measured offset in $\delta^{41}K$ and intensity mismatch. The correlation returns a relationship of $\delta^{41}K \approx 2\text{-}2\times K_{sample}/K_{standard}$ for the pure standard and $\delta^{41}K \approx 2.169\text{-}2.656\times K_{sample}/K_{standard}$ for granite GA. Therefore, a 1% mismatch creates a ≈0.02 ‰ isotopic bias, which is presently a clear limitation in the K isotopic measurements using the Sapphire. It is therefore paramount to analyze the samples with an intensity match within 1% of the bracketing standard to obtain accurate data on the Sapphire, which is the protocol used in this study. As shown below, when the intensities match well, the data obtained on the Sapphire are accurate and precise (<50 ppm). This sensitivity of the $\delta^{41}K$ values to the intensity is most likely due to a combination of the hexapole setup and of the high K background observed on our APEX Omega, over 2 V of K compared to a signal of > 300 V of K for a 150 ppb solution. The K background therefore represents ≈1 ppb of K. It should be noted that the effect reported above is relevant to the instrumental parameters utilized in our study and this may be different for different instrumental parameters.

Effect of matrix elements

The application of standard-sample bracketing method requires column chemistry to isolate K from the matrix elements; therefore, the instrumental mass bias on pure K standards can be assumed to represent that on the bracketed samples. Here we tested the presence of Ca, Na, Rb, Ti, and Cr on the accuracy of K isotopic measurements. The elution interval of K overlaps significantly with that of Rb and Cr on common cation exchange resin (e.g., Chen, et al., 2019; Xu et al., 2019), and residual Ti is identified when using large columns to process low-K samples (Wang and Jacobsen, 2016). While Na and Ca can be completely separated from K, they are common contaminants in the environment, and Na potentially forms molecular interference of $^{23}Na^{16}O^{+}$ at mass 39. Plastic containers made of polyethylene, polyethylene terephthalate, or polypropylene typically have high Ca blanks even after repeated acid cleaning. The presence of Ca is particularly problematic for analysis using the H_2-fed collision cell, whereby a fraction of Ca combines with H to produce CaH^{+} and create an isobaric interference on ^{41}K.

For Ca-doping test, we added various amounts of Sigma-Aldrich Ca (up to 5 % Ca) to pure NIST-SRM 3141a K solutions and then measured them against paired pure NIST-SRM 3141a K solutions at the same K concentration (Figure 5a). All the tests were performed with 150 ppb of K, i.e. that 1 % Ca corresponds to 1.5 ppb of Ca, which on a Faraday cup equipped with a 10^{11} ohm resistor returned ≈2V of ^{40}Ca. A similar approach has been followed to test the effect on a rock sample (granite GH, Figure 5b). The effect is similar on both the pure K standard and on the sample, where the $\delta^{41}K$ correlates with the Ca/K ratio (%) of the solution analyzed with a slope of 0.069. In other words, a Ca/K ratio of 1% (≈2V of ^{40}Ca in our cases for 1.5 ppb of Ca) would affect the $\delta^{41}K$ value by + 0.069 ‰. We therefore suggest that the Ca content in the solution analyzed should always

be kept under 0.3 ppb (400mV on ^{40}Ca in our case). It should be noted that all the samples reported here (except one) had a ^{40}Ca intensity similar to the pure NIST-SRM 3141a solution at 150ppb analyzed as bracketing standard (≈100mV) and therefore did not cause any isobaric interferences. The exception is lunar meteorite LAP 02224, for which ^{40}Ca has an intensity of ≈1V. This sample is prepared at Washington University in St Louis using a large column and hence more acids that likely contribute to the high Ca contents in the purified sample. Giving the relation defined in Figure 5, the presence of Ca in this sample would cause a potential increase its $\delta^{41}K$ by ≈ 0.034 ‰. To minimize Ca contamination, we used Teflon beakers for instrumental analysis.

The other elements (Na, Rb, Cr and Ti) are doped with 1%, 2.5%, 5%, and 10% concentration ratios to that of K (see supplementary tables). These elements produce smaller matrix effects than Ca. Sodium creates the smallest effect of these four elements with ~0.1 ‰ for 10 %, while Na, Rb, and Ti have similar effect ~0.2 ‰ for 10%. In any case, the influence of these elements is negligible if the matrix element concentration is less than 2.5% of that of K. When presented at higher concentrations, Na, Rb, Cr and Ti all cause a shift of $\delta^{41}K$ to lower values (see supplementary table).

Effect of K concentration mismatch

We evaluated the effect of the HNO_3 concentration mismatch between the samples and the standard on the accuracy of the $\delta^{41}K$ as variations in the acid molarity of the analyzed solution had been shown to affect the mass bias for Fe isotopes (Malinovsky et al. 2003). Pure NIST-SRM 3141a K solution were dissolved in HNO_3 at various concentrations (from 1 % to 5 %) and were analyzed against a NIST-SRM 3141a solution dissolved in 3 % HNO_3 (Figure 6). There is a clear correlation (R^2=0.95) between the

$\delta^{41}K$ and the mismatch in HNO_3 concentration. It is therefore important for the accuracy of the measurements to dilute all the samples and standards with the same acid concentrations (Malinovsky et al. 2003; Dauphas et al., 2009). For all the samples analyzed here, samples and standards were prepared from the same bottle of 3 % HNO_3.

Potassium isotopic variations in terrestrial geostandards and a lunar meteorite

The various samples analyzed here covers a $\delta^{41}K$ range of ≈0.6 ‰, with the granite GH being the lightest ($\delta^{41}K$=-0.590±0.018 ‰) and the Hawaiian seawater standard being the heaviest ($\delta^{41}K$=+0.139±0.022 ‰) samples.

The data obtained on the Sapphire compare well with previously published data (see Table 2 and S1 and Figure 7). All samples fall on a slope of 1 line in Figure 7, indicating the consistency in the absolute values obtained on the Sapphire with both a Nu Plasma II and a Neptune plus. This consistency also demonstrates the accuracy of the high-precision data acquired using other instruments from Ku and Jacobsen (2020), Chen et al. (2019), Tuller-Ross et al. (2019), and Tian et al. (2019). For example, the sample that was analyzed the most here and in various literatures, the seawater, returns a $\delta^{41}K$=+0.139±0.022 ‰ (n=12), which is in excellent agreement with the most recent value suggested by Ku and Jacobsen (2020) ($\delta^{41}K$=+0.168±0.014 ‰, n=64), as well as with previously acquired values with lower precisions : $\delta^{41}K$=+0.100±0.305 ‰, (Wang and Jacobsen, 2016), +0.02±0.40 ‰, +0.05±0.70 ‰, +0.12±0.13 ‰ (Li et al., 2016), 0.03±0.70 ‰ (Morgan et al., 2018), +0.12±0.07 ‰ (Wang et al., 2020) and +0.14 ± 0.02 ‰ (Hille et al., 2019).

Furthermore, our data are consistent with the values previously obtained on the Sapphire at Harvard University (see Table S2), for AGV-1 (-0.473±0.043 ‰ vs -0.440±0.012 ‰) and G-2 (-0.470±0.021 ‰ vs -0.420±0.017 ‰).

The lunar meteorite analyzed here was the only sample that had a ^{40}Ca signal higher than the pure K standard (by about 1V, i.e. ≈0.7 ppb of Ca in the measured solution). The data obtained on the Sapphire without correcting for the Ca interference (-0.021 ± 0.034 ‰) as well as after Ca correction using the relation define above (-0.055 ± 0.034 ‰) are fairly consistent with the literature value (-0.01±0.03 ‰, Tian et al., 2020). Therefore, although the Ca content of the lunar sample is resolvable, the data appears to confirm the $\delta^{41}K \approx$ -0.02 ‰ of lunar rocks discovered by Wang and Jacobsen (2016) and later confirmed by Tian et al. (2020). Terrestrial igneous rocks analyzed here and in the literature are systematically lighter by ≈0.4 ‰ (see Figure 8). The heavy isotope enrichment of the lunar basalts for K as well as for other volatile elements such as Zn (e.g., Paniello et al. 2012, Kato et al. 2015), Cl (e.g. Gargano et al. 2020), Ga (Kato and Moynier 2017), and Rb (Pringle and Moynier 2017) is a strong case of an evaporative loss of the volatiles from the Moon and of the presence of a transient lunar atmosphere (Van Kooten et al. 2020).

The excellent agreement between the $\delta^{41}K$ values obtained on the Sapphire in IPGP, Paris on a wide range of previously analyzed samples on different instruments as well as with the two common samples analyzed on the Harvard Sapphire, confirms the accuracy of the high precision K data for the meteorites reported in Ku and Jacobsen (2020) and the remarkable systematic isotopic variation between chondritic samples. Given a factor of 10 improvement in the sensitivity of K isotopic measurements using a

Nu Sapphire, this instrument opens up new applications in cosmochemistry such as the analyses of K-poor samples (e.g. angrite meteorites), meteorite fractions (e.g. chondrules, CAIs) or very precious samples such as future sample returned mission from asteroids, the Moon, and Mars.

Conclusions

We report K isotopic data acquired with a Nu Sapphire dual-path collision cell-capable MC-ICP-MS connected to an Apex Omega for 23 samples, including seawater, terrestrial and lunar rocks that all had been previously analyzed for K isotopes by older generations of mass-spectrometers. We show that K isotopic data acquired using the collision-cell on the Nu Sapphire are both accurate (by comparing our data to published values) and precise (2SD of replicated measurements typically around 0.05 ‰). A major advantage is the high sensitivity of the instrument as the samples can be analyzed in low-resolution mode (≈2000V/ppm of K) and accurate data can be obtained at running concentrations as low as 25 ppb (which for 5 replicates correspond to ≈125 ng of K). This represents a remarkable improvement compared to other methods to analyze small or K-poor samples and will certainly open up new applications. In order to obtain these results, care needs to be taken to 1) avoid the presence of Ca in the K solution (a Ca/K ratio of 1% create a 0.069 ‰ offset), 2) match the concentration of the sample and of the standard (a 1% mismatch create a 0.02 ‰ offset, using our instrumental parameters) as well as the acid molarity of the sample, and 3) well-characterize the instrument behavior and apply correction functions for K and Ca signals. Controlling these factors, the data reported here for 23 geostandards are in good agreement with previous studies using Neptune plus

or Nu Plasma II instruments. This consistency therefore confirms the accuracy of the data that can be obtained on the Sapphire in the future.

Acknowledgements: We thank the two anonymous reviewers for their constructive reviews that greatly improved the quality of the work. We also thank editor Balz Kamber for his comments and efficient handling of our manuscript. F. M. thanks the DIM ACAV+ (Domaine d'Interet Majeur, Astrophysique et Condition d'Apparition de la Vie) of the region Ile de France for providing part of the funding for the Nu Sapphire. F.M. acknowledges funding from the European Research Council under the H2020 framework program/ERC Starting Grant Agreement (#637503-PRISTINE) and financial support of the UnivEarthS Labex program at Sorbonne Paris Cité (#ANR-10-LABX-0023 and #ANR-11-IDEX-0005-02). Parts of this work were supported by IPGP multidisciplinary program PARI.

Figure and Table Captions:

Figure 1. Sapphire dual path design schematic. The low energy path (blue line) is used to analyzed K stable isotopes. See main text for details.

Figure 2: Comparison of the sensitivity of various instruments and techniques used to analyze the K isotopic composition of a pure K standard at 150ppb. The error bar represents the 2SD.

Figure 3: $\delta^{41}K$ as a function of the K concentration (ppb) for the pure K standard SRM3141a (Figure 3a) and for the geostandard DR-N (Figure 3b). Measurements are accurate down to 25ppb.

Figure 4: Effect of the intensity mismatch on the accuracy of the K isotopic composition. The x-axis represents the ratio of the total intensity of the sample and of the standard. The

standard was measured at 150ppb. Figure 4a: Effects on the pure K standard. Figure 4b: Effects on the GA rock standard.

Figure 5: Effect of the Ca content of the solution analyzed on the accuracy of the K isotopic composition. The x-axis represents the Ca content of the solution with regards to the K concentration (150ppb for all samples) in %. Figure 5a corresponds to the pure NIST SRM3141a standard and Figure 5b corresponds to the GH rock standard. The slope is similar in both cases (0.069) and therefore 1% Ca/K ratio biased the $\delta^{41}K$ by +0.069 ‰.

Figure 6: Effect of HNO_3 concentration mismatch between sample and standard on the $\delta^{41}K$ values. The "sample" here represents the pure NIST SRM3141a standard dissolved in acid at various molarity from 1% to 5% HNO_3. The bracketing standard is a pure NIST SRM3141a solution in 3% HNO_3. There is a clear effect of the mismatch of acid molarity on the accuracy of the $\delta^{41}K$.

Figure 7: $\delta^{41}K$ values from the literature (see Table 2) reported against $\delta^{41}K$ values obtained here on the Nu Sapphire. The dotted line represents a straight line with a slope 1. Most samples fall on the slope 1 line and confirms that the data obtained on the Sapphire are consistent with literature values.

Figure 8: $\delta^{41}K$ values of the different samples reported here. The lunar basaltic meteorite (LAP 02224) is isotopically heavier than all terrestrial rocks.

Table 1. Operating parameters of the Sapphire instrument and the Apex Omega introduction system.

Table 2: Potassium isotopic data of the various rock samples analyzed here. The literature data are all from Xu et al. (2019) except for FK-N (Chen et al., 2019) and LAP 02224 (Tian et al., 2020).

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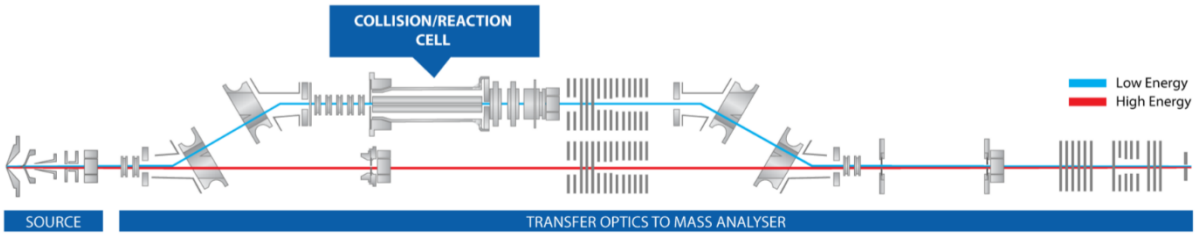
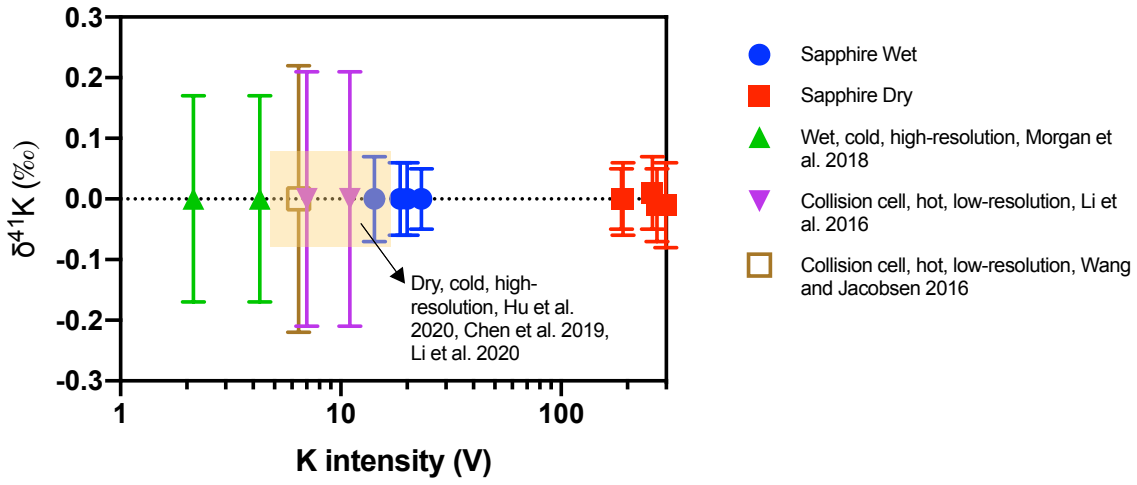
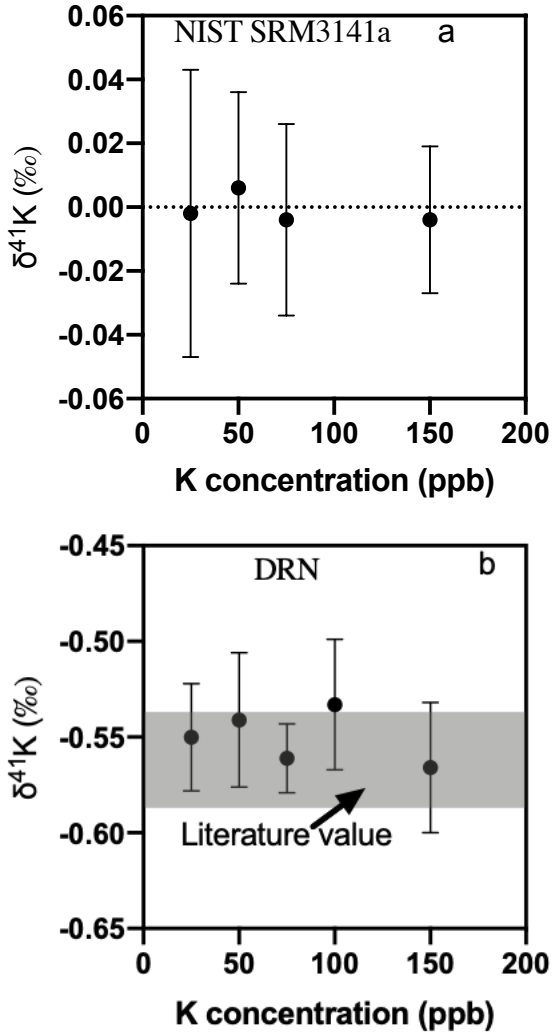
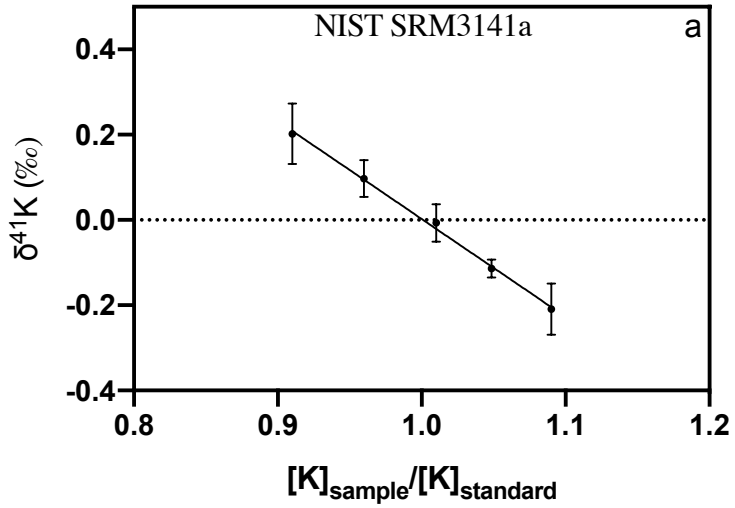
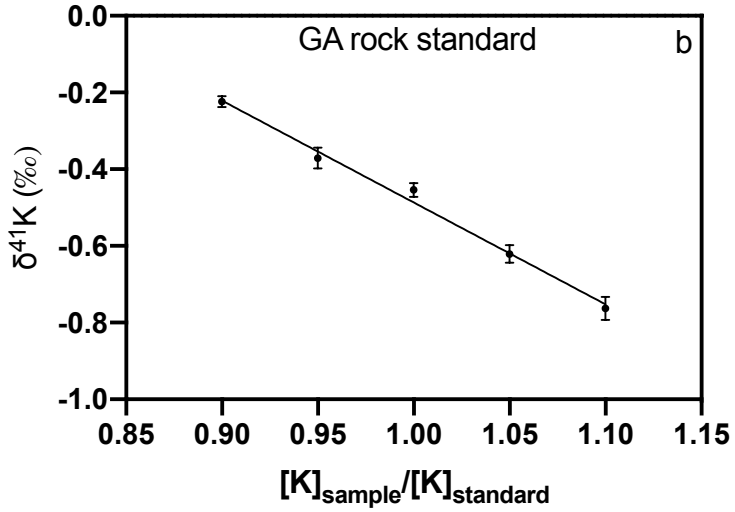

COLLISION/REACTION CELL
Low Energy
High Energy
SOURCE
TRANSFER OPTICS TO MASS ANALYSER


0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
δ41K (‰)
1
10
100
K intensity (V)
Dry, cold, high-resolution, Hu et al. 2020, Chen et al. 2019, Li et al. 2020
Sapphire Wet
Sapphire Dry
Wet, cold, high-resolution, Morgan et al. 2018
Collision cell, hot, low-resolution, Li et al. 2016
Collision cell, hot, low-resolution, Wang and Jacobsen 2016


NIST SRM3141a
a
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
δ41K (‰)
0
50
100
150
200
K concentration (ppb)
DRN
b
-0.45
-0.50
-0.55
-0.60
-0.65
δ41K (‰)
Literature value
0
50
100
150
200
K concentration (ppb)


NIST SRM3141a
a
0.4
0.2
0.0
-0.2
-0.4
δ41K (‰)
0.8
0.9
1.0
1.1
1.2
[K]sample/[K]standard


GA rock standard
b
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
δ41K (‰)
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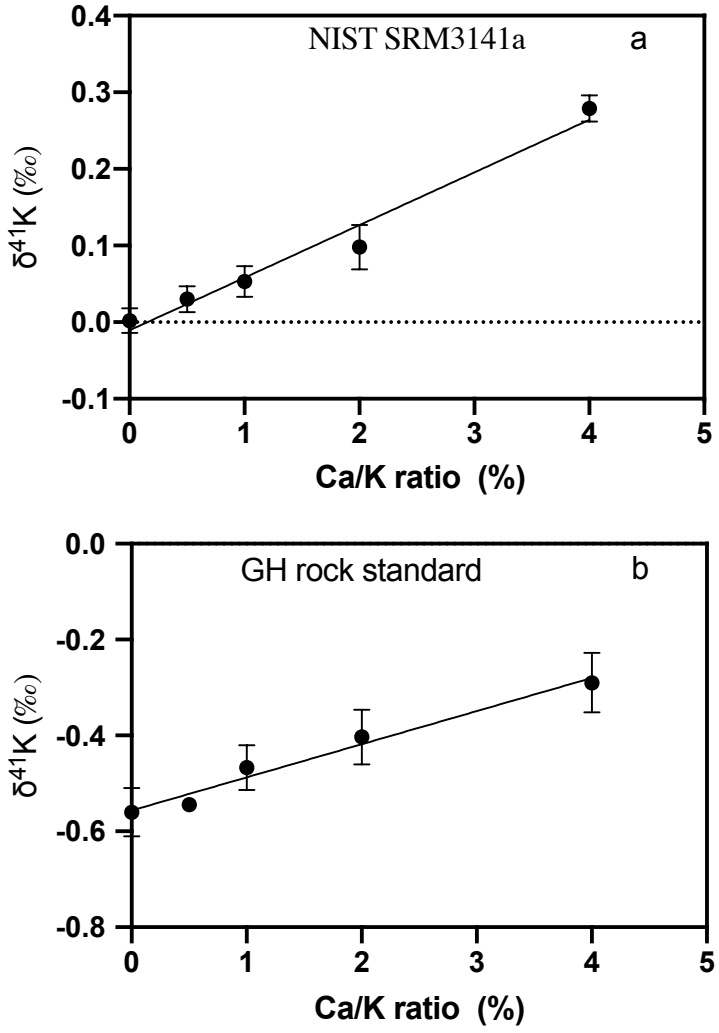
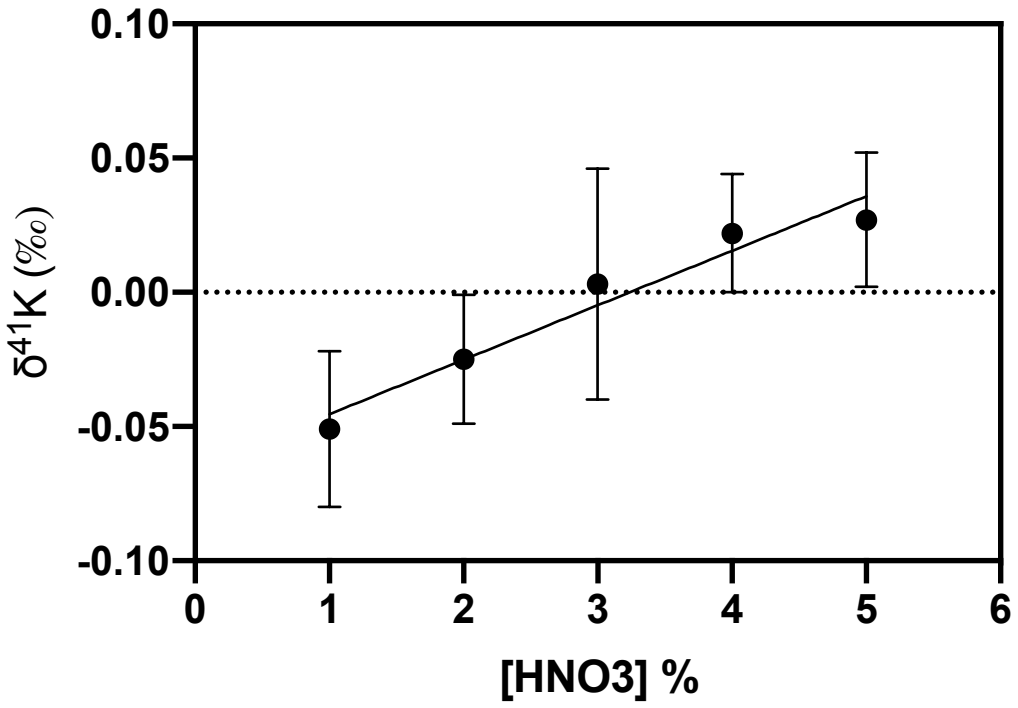
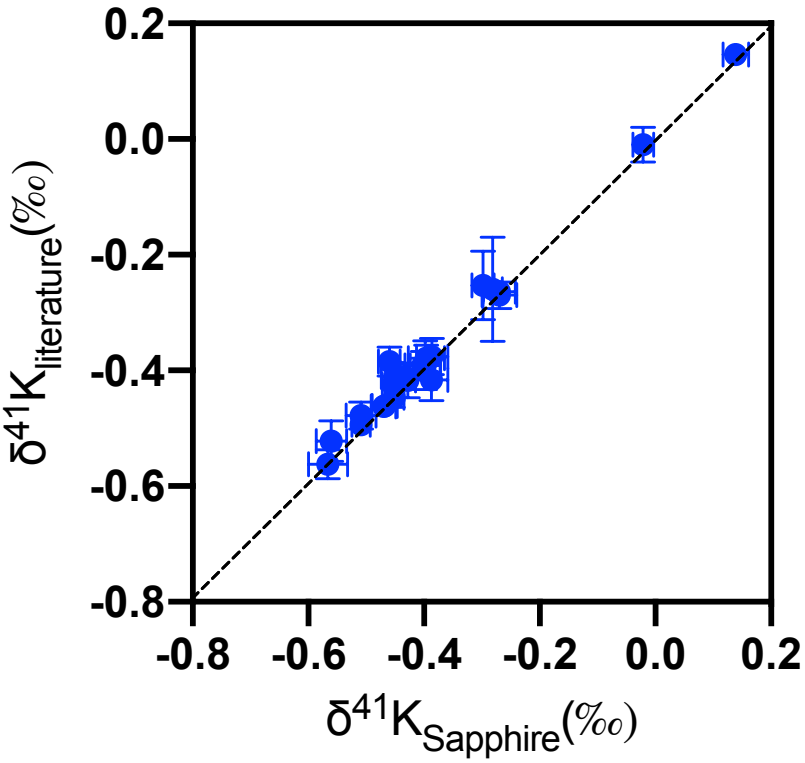
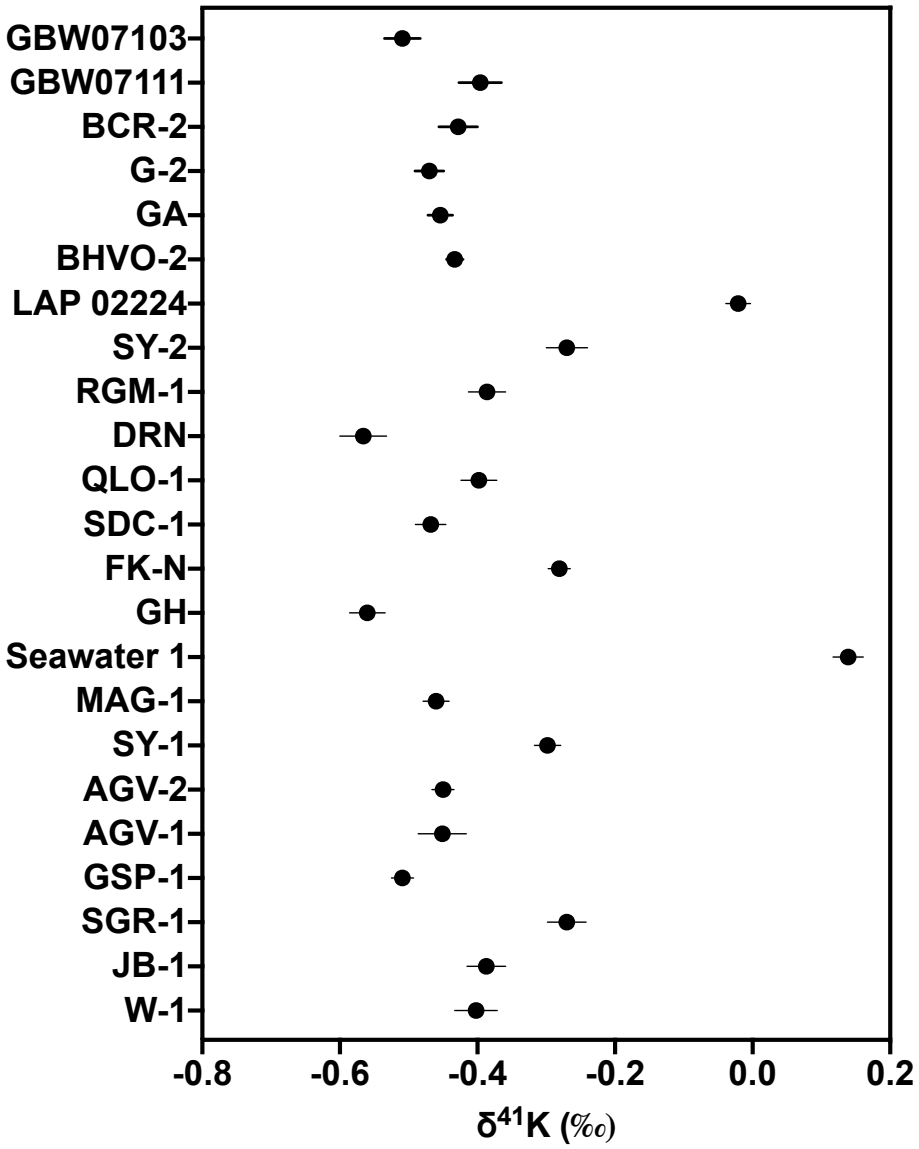
0.90
0.95
1.00
1.05
1.10
1.15
[K]sample/[K]standard


NIST SRM3141a
a
0.4
0.3
0.2
0.1
0.0
-0.1
δ41K (‰)
0
1
2
3
4
5
Ca/K ratio (%)
GH rock standard
b
0.0
-0.2
-0.4
-0.6
-0.8
δ41K (‰)
0
1
2
3
4
5
Ca/K ratio (%)


0.10
0.05
0.00
-0.05
-0.10
δ41K (‰)
0
1
2
3
4
5
6
[HNO3] %


0.2
0.0
-0.2
-0.4
-0.6
-0.8
-0.8
-0.6
-0.4
-0.2
0.0
0.2
δ41KSapphire(‰)
δ41Kliterature(‰)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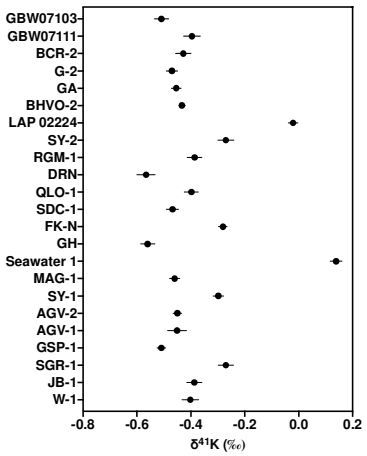
BCR-2
G-2
GA
BHVO-2
LAP 02224
SY-2
RGM-1
DRN
QLO-1
SDC-1
FK-N
GH
Seawater 1
MAG-1
SY-1
AGV-2
AGV-1
GSP-1
SGR-1
JB-1
W-1
-0.8
-0.6
-0.4
-0.2
0.0
0.2
δ41K (‰)

Nu Sapphire Instrument Setting utilized in this study	
RF Power	1300 W
Coolant gas flow rate	13 L/min
Auxiliary gas flow	0.75-0.9 L/min
Sampler/skimmer cone material	Ni
He collision gas flow	2-3 sccm
H_2 reaction gas flow	5 sccm
Quad 1	18.4
Quad 2	-43.0
Apex parameters	
Argon Sweep Gas Flow	2.18-3.42 L/min
Nebulizer pressure	27.4-29.0 psi
Peripump Speed	17.0 (rpm)
Peripump Flow	600.0 (µL/min)
Nebulizer uptake rate	50 or 100 µL/min
Peltier Cooler temperature	3.0 ºC
Desolvator temperature	155.0 ºC
Spray chamber temperature	140 ºC

Sample	Type	$\delta^{41}K$ (‰)	2SD	95%c.i.	N	$\delta^{41}K$ (‰) literature	95%c.i.	95%c.i. std	Chemical preparation
W-1	Diabase	-0.402	0.058	0.031	6	-0.391	0.024	0.038	UW
JB-1	Basalt	-0.387	0.053	0.028	6	-0.416	0.036	0.038	UW
BCR-2	Basalt	-0.428	0.028	0.013	7	-0.417	0.030	0.036	IPGP
BHVO-2*	Basalt	-0.434	0.04		11	-0.411	0.011	0.017	IPGP
AGV-1	Andesite	-0.451	0.035	0.016	7	-0.447	0.017	0.027	UW
AGV-2	Andesite	-0.450	0.034	0.016	7	-0.410	0.020	0.033	IPGP
QLO-1	Quartz Latite	-0.398	0.049	0.026	6	-0.391	0.042	0.038	UW
DR-N	Diorite	-0.566	0.066	0.034	6	-0.562	0.025	0.042	UW
GSP-1	Granodiorite	-0.509	0.035	0.016	7	-0.494	0.016	0.036	UW
	duplicate	-0.495	0.058	0.030	6			0.041	UW
GBW07111	Granodiorite	-0.396	0.059	0.031	6	-0.379	0.023	0.044	UW
G-2	Granite	-0.470	0.039	0.021	6	-0.462	0.014	0.040	UW
GH	Granite	-0.560	0.050	0.026	6	-0.522	0.035	0.039	UW
GA	Granite	-0.454	0.034	0.018	6	-0.425	0.023	0.043	UW
GBW07103	Granite	-0.509	0.056	0.026	7	-0.478	0.023	0.038	UW
RGM-1	Rhyolite	-0.386	0.051	0.027	6	-0.376	0.031	0.044	UW
SY-1	Syenite	-0.298	0.046	0.019	8	-0.253	0.059	0.032	UW
SY-2	Syenite	-0.273	0.069	0.032	7	-0.270	0.023	0.038	UW
SGR-1	Shale	-0.270	0.061	0.028	7	-0.264	0.015	0.036	UW
MAG-1	Marine Mud	-0.460	0.037	0.019	6	-0.385	0.025	0.024	UW
SDC-1	Mica Shist	-0.468	0.048	0.022	7	-0.461	0.017	0.033	UW
FK-N	K-Felspar	-0.281	0.031	0.016	6	-0.26	0.09	0.024	UW
FK-N IPGP		-0.303	0.054	0.025	7			0.033	IPGP
Seawater	Water	0.139	0.075	0.024	12	0.146	0.018	0.019	UW
	replicate	0.130	0.070	0.032	7			0.033	UW
LAP 02224	Lunar	-0.021	0.034	0.018	6	-0.01	0.03	0.024	WU

***BHVO-2 has been used to estimate the long-term reproducibility evaluated over the course of 11 sessions and three separate chemical procedures (see Table S1 for the details of the measurements).**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GBW07111
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G-2
GA
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DRN
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SDC-1
FK-N
GH
Seawater 1
MAG-1
SY-1
AGV-2
AGV-1
GSP-1
SGR-1
JB-1
W-1
-0.8
-0.6
-0.4
-0.2
0.0
0.2
δ41K (‰)