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A novel method for extracting potassium (K) from K-poor and sodium-rich samples for high-precision stable K isotope analysis†

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Reconstruction of stable potassium isotope composition ($^{41}\text{K}/^{39}\text{K}$) in ancient seawater has significant implications for our understanding of the fundamental controls on the long-term stability of Earth's climate and ocean chemistry, but the relevant research is hampered by scarce preservation of seawater K in geological records. Marine halite (NaCl) samples are potentially valuable archives of seawater K isotope signatures because they often contain abundant fluid inclusions directly sourced from evaporated ancient seawater. However, the extremely high Na matrix relative to low K concentrations in halite presents a formidable challenge for K isotope analysis. This study reports a novel and efficient K extraction method that can separate K from a high Na matrix by precipitating K as a sparsely soluble salt using sodium tetraphenylborate (TPB). Development of this method was based on an in-depth understanding of the TPB precipitation reaction and solubility equilibrium of relevant TPB salts. Key parameters, including reaction time, precipitate recovery and rinse, and further K purification for isotope analysis, have been optimized through extensive laboratory experiments. It is demonstrated that this new method can extract small quantities of K down to 20 μg from a large quantity of the NaCl matrix up to 1 gram. In addition, preliminary results show that this new extraction method can be also applied to prepare carbonate samples, which represent another important type of sample pertinent to K isotope research, notoriously difficult to analyze due to their low K concentrations and high Ca matrices. For the first time, this study demonstrates the utility of TPB chemistry in preparing challenging K-poor, matrix-rich samples for high-precision stable K isotope analysis.

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1. Introduction

It has been hypothesized that the long-term stability of Earth's climate over geological timescales is controlled by silicate weathering and marine authigenic clay formation.^{1–3} The former process involves chemical reactions between silicate minerals and carbonic acid, and this process removes carbon dioxide (CO_2) from the atmosphere, and it also delivers alkalinity and other soluble ions to the ocean.⁴ On the other hand, formation of authigenic clay minerals in the ocean consumes seawater alkalinity, fixes soluble ions into clay structures, and releases CO_2 back to the atmosphere.^{5,6} Based on geochemical models, it can be demonstrated that climate and seawater chemistry (e.g., pH) on Earth is less susceptible to changes induced by major climate perturbations, such as CO_2 release from volcanism, only when the two processes can work in tandem.¹ Despite the evidence from models, field evidence that directly constrains the balance between global silicate

weathering and marine authigenic clay formation over Earth's history remains scarce, leaving modelling results largely untested.

Stable K isotope composition ($^{41}\text{K}/^{39}\text{K}$, typically expressed as $\delta^{41}\text{K}$) of seawater has a unique bearing on the balance between global silicate weathering and marine authigenic clay formation.^{7,8} Stable K isotopes have emerged recently as a novel geochemical tracer for the silicate cycle because K primarily resides in silicate minerals rather than carbonates. An intriguing $\delta^{41}\text{K}$ spread of more than 3‰ has been reported for samples collected from low-temperature environments.⁸ Of particular interest is a $\sim 0.6\text{‰}$ difference in $^{41}\text{K}/^{39}\text{K}$ between modern seawater and the bulk silicate Earth (BSE); seawater has a homogeneous $\delta^{41}\text{K}$ value of 0.13‰,^{9,10} whereas the BSE is characterized by a considerably lower $\delta^{41}\text{K}$ value of -0.45‰ .^{11,12} Due to the long residence time of K in seawater (i.e., ~ 10 million years),¹³ seawater $\delta^{41}\text{K}$ reflects the isotope mass balance between major K sources and sinks in the ocean. Major K sources in the ocean include high-temperature hydrothermal fluids and the riverine input, and the latter is closely related to silicate weathering on land. The global average $\delta^{41}\text{K}$ values of high-temperature hydrothermal fluids and the riverine input are estimated to be $\sim -0.35\text{‰}$ for both, only slightly higher than

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the BSE value.^{7,14–16} Therefore, these two K sources are insufficient to explain the high $\delta^{41}\text{K}$ value of modern seawater. Authigenic clay formation in marine sediments and during low-temperature hydrothermal alteration of the oceanic crust is a major K sink in the ocean. Because field and laboratory evidence indicated preferential incorporation of light K isotopes in clay crystal lattices,^{17–20} marine authigenic clay formation provides a viable mechanism essential in producing the high $\delta^{41}\text{K}$ value of modern seawater. If the balance between silicate weathering and marine authigenic clay formation has shifted throughout Earth's history, it should cause corresponding variations in seawater $\delta^{41}\text{K}$ over time.

Reconstruction of ancient seawater $\delta^{41}\text{K}$, therefore, can provide crucial field evidence needed to test the role of silicate weathering and marine authigenic clay formation in the climate system. However, this task is extremely challenging, because of sparse preservation of seawater K in geological archives. Several types of geological archives have been examined so far to assess their potential in shedding light on ancient seawater $\delta^{41}\text{K}$. Marine biogenic carbonates (*e.g.*, foraminifera and corals) are one of the most commonly used archives for reconstruction of chemical composition of ancient seawater, but K isotope fractionation during the incorporation of seawater K into biogenic carbonates appears to be quite complicated and is not yet understood,^{21,22} making it difficult to use biogenic carbonates to reconstruct $\delta^{41}\text{K}$ of ancient seawater at the moment. Ophiolites, the ancient oceanic crust that was hydrothermally altered by ancient seawater and subsequently obducted onto land, represent another possible archive to constrain seawater $\delta^{41}\text{K}$ in the past, but interpretation of $\delta^{41}\text{K}$ data from ophiolites remains ambiguous due to a lack of detailed knowledge on K isotope fractionation during various hydrothermal reactions.^{7,23,24} In addition, marine authigenic clay minerals can potentially shed light on ancient seawater $\delta^{41}\text{K}$, but published studies indicated different K isotope fractionations associated with different types of clay minerals,^{19,25} highlighting the necessity to separate individual clay minerals from bulk sediments for unambiguous reconstruction of seawater $\delta^{41}\text{K}$. Separation of specific authigenic clay minerals from detrital clays in marine sediments, however, is difficult and has not been performed for K isotope measurement yet. Potassium salts found in marine evaporites, such as sylvite and carnallite, may also help constrain ancient seawater $\delta^{41}\text{K}$,^{26,27} but these K salts are highly soluble. Therefore, their occurrence in geological records in Earth's history is rather rare.

One geological archive that has never been explored to date is fluid inclusions in marine halite (NaCl). Halite is a common mineral found in marine evaporite sequences, and it is a particularly important archive that shows great promise to constrain ancient seawater $\delta^{41}\text{K}$ for several reasons. First, the occurrence of halite in geological records is more common than that of K salts,²⁸ and samples with confirmed marine origins are available for the entire Phanerozoic.^{28,29} Second, aqueous K ions are only weakly partitioned into carbonates and gypsum, the two phases formed before halite precipitation during seawater evaporation, whereas halite formation precedes precipitation of major K salts.^{28,30} As a result, fluid inclusions in halite may

directly preserve unaltered seawater K isotope composition without any K isotope fractionation.

Nonetheless, assessment of the true potential of fluid inclusions in marine halite in recording seawater $\delta^{41}\text{K}$ is presently prohibited by a substantial analytical hurdle: the separation of a small quantity of K in halite samples from the bulk NaCl matrix. High-precision stable K isotope analysis became possible by using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) only a few years ago.^{12,31,32} For such analyses, it is imperative to purify K from Na to avoid Na-induced matrix effects that can lead to inaccurate K isotope measurements by MC-ICP-MS.^{33–35} Because neither *in situ* analysis nor physical separation of individual fluid inclusions from bulk samples is feasible for high-precision K isotope analysis owing to the small volume (and hence K mass) of individual primary fluid inclusions in marine halite,³⁶ it is mandatory to analyze bulk halite samples. Potassium concentrations in bulk halite samples, especially ancient ones, are low, often ranging from ~ 20 to a couple of hundred $\mu\text{g g}^{-1}$.³⁰ This means that successful K isotope analysis of bulk halite samples would require separation of K from a Na-rich matrix with exceedingly high Na/K molar ratios in the 10^3 to 10^4 range, significantly higher than the Na/K ratios of any samples analyzed for K isotopes so far. Because Na and K are both alkali metals and they behave similarly on cation exchange resin (*e.g.*, AG50W-X8 or -X12) commonly used to separate these two elements for K isotope measurements,^{33,34,37,38} extremely high Na/K ratios of halite samples present a formidable challenge.

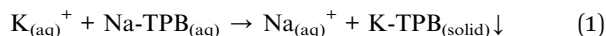
This study presents a novel method that can extract μg -level K from a gram-level of the NaCl matrix. After extraction, the samples can be successfully purified by the existing chromatographic separation protocol for high-precision stable K isotope analysis. It is demonstrated here that this method can extract as little as $20 \mu\text{g}$ K from at least 1 gram of NaCl. This quantity of extracted K is sufficient for high-precision K isotope analysis by the conventional high mass resolution MC-ICP-MS,^{37,39} and more than sufficient for analysis by the latest collision-cell MC-ICP-MS that has a higher sensitivity for K.^{33,34,40} As a result, this new method essentially enables any laboratories that have established high-precision K isotope analysis on MC-ICP-MS to study natural halite samples, thereby potentially advancing research on reconstructing $\delta^{41}\text{K}$ in ancient seawater and elucidating the fundamental controls on Earth's climate from silicate weathering and marine authigenic clay formation. Additionally, preliminary results are provided here to demonstrate the potential of extending this extraction method to carbonates – another type of sample that holds significant interest for stable K isotope research, but challenging to analyze due to their low K concentrations and high Ca matrices.^{21,22,41}

2. Experimental section

2.1 Design of the K extraction method for K isotope analysis

2.1.1 Theoretical considerations. The basic idea of separating K from a high Na (or other cations) matrix was inspired by early gravimetric and turbidimetric measurements of K concentrations.^{42–46} During these analyses, soluble K ions were

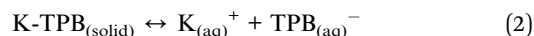
converted into white potassium tetraphenylborate (K-TPB, chemical formula: $\text{KB}(\text{C}_6\text{H}_5)_4$) precipitates by a precipitating reagent, often sodium tetraphenylborate (Na-TPB, chemical formula: $\text{NaB}(\text{C}_6\text{H}_5)_4$). This relied on the following chemical reaction:



where Na-TPB is a precipitating reagent, and K-TPB is a solid with low solubility in water.⁴⁷ Subsequently, K concentrations were quantified either by weighing the precipitated K-TPB solids,^{42–44} or by measuring the turbidity of the K-TPB suspensions.^{45,46} However, these published precipitation protocols were developed exclusively for K concentration measurement with percent-level precision. Moreover, they were often employed to handle large sample sizes of a few milligrams of K. Therefore, none of the existing precipitation protocols could be directly applied for preparing significantly smaller samples (*i.e.*, $\leq 100 \mu\text{g K}$) for stable K isotope analysis. The isotopic analysis requires more stringent sample preparation in terms of the K yield, blank, and level of matrix removal to achieve measurements that have more than two orders of magnitude higher precision as compared to the target precision of K concentration analysis. Hence, there is a need to develop a new protocol that can be effective in extracting small quantities of K from K-poor, matrix-rich samples for high-precision K isotope analysis.

Quantitative conversion of K in a sample into K-TPB solids is a prerequisite for an effective sample preparation method for K isotope analysis. The amount of Na-TPB salt required to fully react with a known amount of K can be easily calculated based on the chemical stoichiometry depicted in eqn (1). Upon completion of the precipitation reaction, the amount of dissolved K ions remaining in the sample solution will be determined by the solubility of the reaction product – K-TPB. The solubility of K-TPB in water at room temperature (25 °C) is $1.76 \times 10^{-4} \text{ mol L}^{-1}$,⁴⁷ equivalent to $\sim 7 \mu\text{g per g K}$. Although this solubility is sufficiently low and can be ignored during gravimetric or turbidimetric measurements of K concentrations that use large sample sizes at the milligram level, it is too high to be ignored when the goal is to extract a total of $\leq 100 \mu\text{g K}$ from a sample for K isotope analysis.

Solubility equilibrium of K-TPB, therefore, must be considered to devise an effective strategy to minimize soluble K ions remaining in the solution. K-TPB solubility equilibrium can be expressed by:



The aqueous K concentration is governed by the concentration of TPB^- anions in the solution and the K-TPB solubility product constant ($K_{\text{sp_K-TPB}}$) through the following relation:

$$K_{\text{sp_K-TPB}} = [\text{K}^+][\text{TPB}^-] \quad (3)$$

Although 100% conversion of K cations into K-TPB solids is not possible, it is evident from eqn (3) that soluble K ions can be suppressed by addition of Na-TPB in excess to maintain a high

$[\text{TPB}^-]$ concentration in the solution after the TPB precipitation reaction.

Combining the chemical stoichiometry of the TPB reaction (eqn (1)) and K-TPB solubility equilibrium (eqn (2)), the amount of Na-TPB salt required to achieve a designated yield of K-TPB precipitation for a given K mass can be calculated. Because dissolution of halite samples targeted by this study is expected to produce Na-rich sample solutions with relatively high ionic strength, it is crucial to consider the ionic strength of the solution during the calculations. To account for solution ionic strength, activities instead of concentrations should be considered for K-TPB solubility equilibrium, and hence eqn (3) can be rewritten as:

$$K_{\text{sp_K-TPB}} = (\gamma_{\text{K}^+}[\text{K}^+])(\gamma_{\text{TPB}^-}[\text{TPB}^-]) \quad (4)$$

where γ_{K^+} and γ_{TPB^-} represent the activity coefficient for K and TPB ions, respectively. Previous studies showed that activity coefficients of different ions, including K^+ , Na^+ , and TPB^- , in a Na–K-TPB system can all be described by using the following equation:⁴⁸

$$\gamma = a \times I^3 + b \times I^2 + c \times I + d \quad (5)$$

where I indicates the ionic strength of a solution, and a , b , c , and d are constants constrained by combined thermodynamic calculations and laboratory experiments.⁴⁸ Each type of ion (*i.e.*, K^+ , Na^+ , and TPB^-) has its own set of a , b , c , and d values, and these values are provided in Table S1 of the ESI.† The K-TPB solubility product constant in water at different temperatures has been compiled previously,⁴⁷ and the recommended $K_{\text{sp_K-TPB}}$ value at 25 °C (*i.e.*, $3 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$) was used in the calculations presented below.

Theoretical calculations have revealed that the solution ionic strength and volume have significant influences on the yield of K-TPB solids. First, K-TPB precipitation at room temperature is more effective in a solution with a higher ionic strength (Fig. 1a), because the TPB^- activity coefficient increases sharply with increasing ionic strength of the solution whereas the K^+ activity coefficient decreases slightly (ESI Fig. S1†). This behavior highlights that the TPB salt is uniquely advantageous in extracting K from high salinity solutions. For a given K solution, the amount of Na-TPB salt required to achieve the same degree of K precipitation in a high ionic strength solution is less than that required in a low ionic strength solution, and the difference in Na-TPB consumption becomes especially significant when a high K precipitation yield (*e.g.*, $>99.5\%$) is targeted (Fig. 1a). These results suggest that the K extraction should be conducted at relatively high ionic strength.

Second, the K extraction efficiency is also strongly affected by the volume of the solution in which the K-TPB precipitation reaction occurs (Fig. 1b). For a given K mass within the range targeted in this study (*i.e.*, 20–100 $\mu\text{g K}$), the amount of Na-TPB needed to achieve the same degree of K precipitation generally increases with the volume of the solution, and this increase is particularly significant when a high yield of K-TPB solids is needed (Fig. 1b). This is because K-TPB solubility equilibrium,

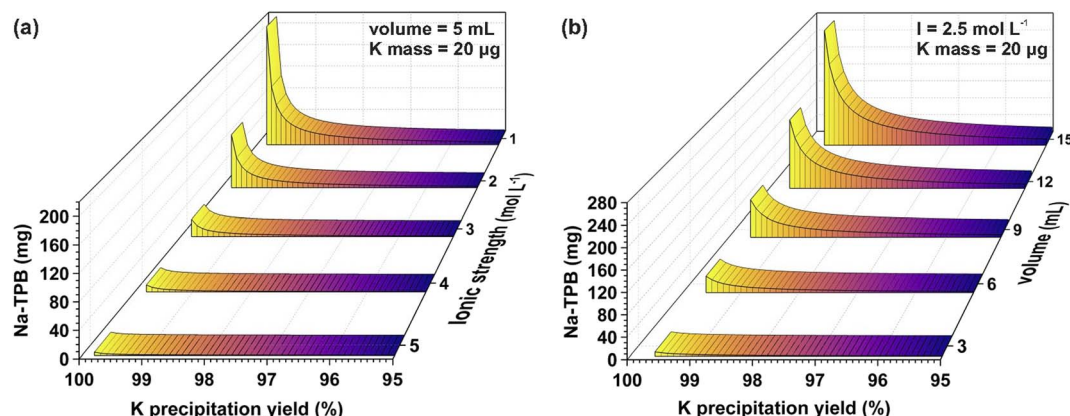


Fig. 1 Calculated Na-TPB consumption for K-TPB precipitation in solution with different ionic strengths (a) and different volumes (b).

rather than the chemical stoichiometry of eqn (1), is the primary control on the yield of K-TPB solids during the extraction of small quantities of K. As the volume of the solution increases, more Na-TPB salt is needed to maintain the same $[TPB^-]$ concentration. Otherwise, K-TPB solubility equilibrium would shift towards dissolution as dictated by eqn (2). In practice, this means if the volume of the solution is too large, the required amount of Na-TPB salt to achieve a sufficiently high K yield, even for a small quantity of K, may become impractically large. For example, extracting 99% of K from a 25 mL fresh solution that contains 20 μg K would require >1 gram of Na-TPB salt. Therefore, K extraction should be performed in a solution with the smallest possible volume, preferably, less than 10 mL.

2.1.2 A practical protocol for K-TPB precipitation. Although the amount of Na-TPB salt required to achieve a designated degree of K-TPB precipitation can be calculated individually for each sample, it is more convenient in practice to establish a standardized protocol applicable to different samples. One

protocol is developed and reported here. In this protocol, bulk halite samples are dissolved in water to different volumes to produce sample solutions at a constant ionic strength of 2.5 mol L^{-1} . Although it is possible to produce sample solutions at a higher ionic strength of up to ~ 6 mol L^{-1} , as determined by the NaCl solubility at 25 $^{\circ}\text{C}$,⁴⁹ and K-TPB precipitation is more efficient in solution with higher ionic strength, it was observed that ionic strength being too high could cause almost instant “salting-out” of Na-TPB upon addition of the precipitating reagent into the sample solution (details in Section 3.1), resulting in low K yield. Therefore, a lower ionic strength of 2.5 mol L^{-1} was chosen. Precipitation of K-TPB is induced by adding 0.5 mol per L Na-TPB solution to sample solutions.

A lookup plot is presented to illustrate the volume of 0.5 mol per L Na-TPB solution required to achieve near-quantitative ($\geq 99\%$) precipitation of 20 μg K at different matrix levels of up to 1 gram NaCl (Fig. 2a). Three important features were discovered with implications for the implementation of the K

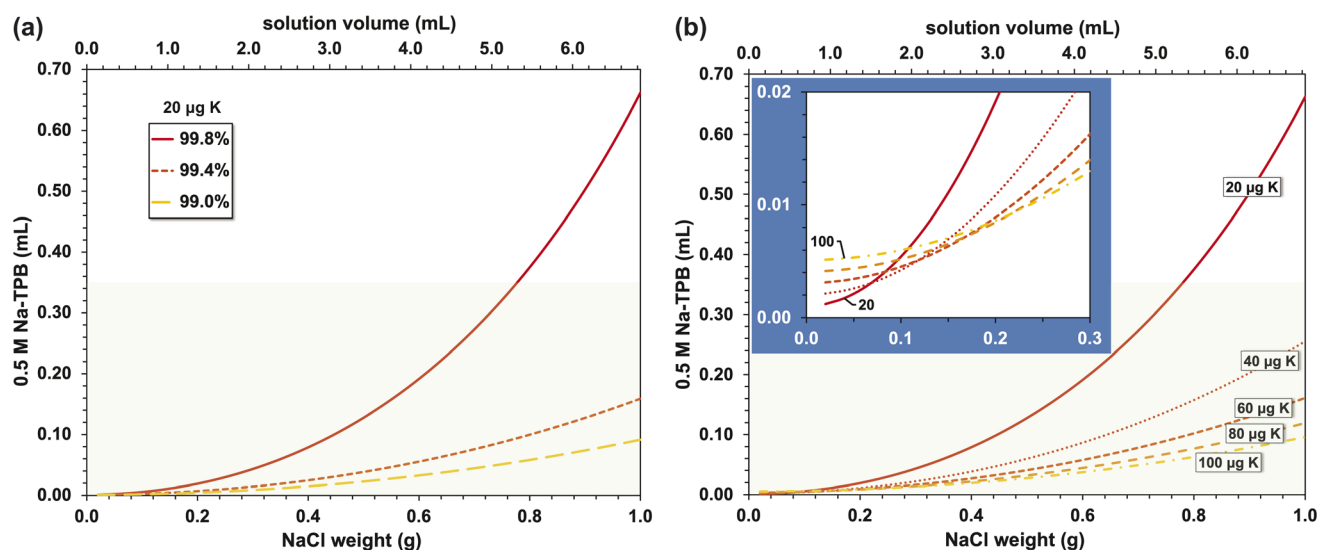


Fig. 2 The volume of 0.5 mol per L Na-TPB solution required to precipitate 20 μg K from different Na matrix levels at a constant solution ionic strength of 2.5 mol L^{-1} (a); and the volume of 0.5 mol per L Na-TPB solution required to precipitate 99.8% of K of different quantities ranging from 20 to 100 μg K from varying Na matrix levels at a constant solution ionic strength of 2.5 mol L^{-1} (b). As shaded in green, a constant volume of 0.35 mL of 0.5 mol per L Na-TPB solution was utilized in this study.

extraction protocol. First, as the NaCl matrix level (and hence the solution volume) increases, more Na-TPB solution is needed to yield the same degree of K-TPB precipitation for samples containing the same amount of K (Fig. 2a). Second, as the NaCl matrix level increases, the volume of 0.5 mol per L Na-TPB solution required to achieve a high degree of K-TPB precipitation becomes disproportionately higher as compared to the volume required to achieve a lower degree of K-TPB precipitation at the same matrix level (Fig. 2a). Lastly, when the bulk NaCl mass is larger than ~ 0.1 g, the volume of 0.5 mol per L Na-TPB required to produce a high yield of K-TPB precipitates in a sample containing 20 μg K is larger than that required to produce the same degree of K-TPB precipitation in a sample containing >20 μg K at the same matrix level (Fig. 2b). All these features once again highlight the dominant control of K-TPB solubility equilibrium during the extraction of small quantities of K from Na-rich samples. Although the chemical stoichiometry of eqn (1) becomes the dominant control on the Na-TPB usage when the sample matrix level is low (*i.e.*, $<\sim 0.1$ g NaCl) (Fig. 2b), these samples would have high enough K/Na ratios that generally can be directly processed by the conventional chromatographic separation without the K extraction reported here.

Based on the features described above, it can be concluded that a 1 g NaCl bulk sample containing a total of 20 μg K represents the most challenging case as shown in Fig. 2 to prepare for K isotope analysis, and a volume of 0.5 mol per L Na-TPB solution capable of producing sufficiently high K-TPB precipitation in this case should be also effective in preparing samples containing a higher amount of K at the same or lower Na matrix levels. As a result, a constant 0.35 mL 0.5 mol per L Na-TPB solution was used during this study. Theoretically, this amount of Na-TPB solution is sufficient to extract nearly all K ($\sim 99.5\%$ or more) from any samples with a total amount of K ranging from 20 μg to up to ~ 7 mg and a matrix level as high as 1 g NaCl. This approach simplifies the extraction process and has been demonstrated to be effective (details in Section 3.7).

2.2 Reagents and materials

Ultrapure water (18.2 M Ω cm), produced by a Milli-Q IQ 7000 water purification system (MilliporeSigma, MA, USA), was used in this study. Acids (HNO₃ and HCl) were either purchased directly from Fisher Chemical (Optima™ grade, NJ, USA) or produced in-house by distillation of trace-metal grade acids using a Teflon DST-1000 acid purification system from Saville (MN, USA). Acetone (Optima™ grade) was purchased from Fisher Chemical. Powdered sodium chloride (trace metal basis, 99.999%) and Na-TPB (ACS grade, $\geq 99.5\%$) were purchased from Sigma-Aldrich (MA, USA). Calcium carbonate powders (trace metal basis, 99.999%) were purchased from Alfa Aesar (MA, USA). All containers, pipette tips, and filters used in this study were acid-cleaned and then thoroughly rinsed with Milli-Q water prior to use.

To prepare the 0.5 mol per L Na-TPB precipitating reagent, Na-TPB salt was first weighed on an analytical balance into a pre-cleaned Teflon beaker and then dissolved in Milli-Q water.

The solution was left for several hours to ensure complete dissolution of Na-TPB salt. Any insoluble particulate materials in the solution were removed by filtration using a 25 mm syringe filter with a 0.2 μm PTFE membrane. Since no K isotope composition has been reported for any natural halite samples, and no halite standard with a certified K isotope composition exists, the new method in this study was validated using a synthetic “halite” (NaCl) solution doped with different quantities of K with a known K isotope composition. The synthetic halite stock solution had an ionic strength of 5 mol L⁻¹ and was prepared by dissolving trace-metal grade NaCl salt in Milli-Q water. A synthetic “carbonate” (CaCl₂) solution with a high ionic strength near CaCl₂ saturation was also prepared. The trace-metal grade calcium carbonate powders were fully dissolved in HCl, and the solution was then evaporated to complete dryness at ~ 160 °C on a hotplate. The resulting CaCl₂ salt was weighed and then dissolved in Milli-Q water to make the synthetic carbonate stock solution. The in-house high-purity K standard solution (*i.e.*, UMN-K) was used as the K source added to the synthetic halite and carbonate solutions, because it has a well-constrained $\delta^{41}\text{K}$ value of $0.43\text{‰} \pm 0.04\text{‰}$ (2SD, $n = 187$), based on repeated analyses in my laboratory in the past two years. Different aliquots of UMN-K solution were first dried on a hotplate and then re-dissolved in different aliquots of the synthetic halite or carbonate solution, followed by further dilution of the solution to any desired ionic strength by Milli-Q water to produce the final test samples used in various experiments of this study.

2.3 Instrumentation and measurements

Stable K isotope ratios were measured by using a collision-cell equipped MC-ICP-MS (model name: “Sapphire”, Nu Instruments, Wrexham, UK) at the Department of Earth and Environmental Sciences, University of Minnesota-Twin Cities. This instrument features a dual-ion-path design, including a high-energy (HE) path with a 6 kV acceleration voltage and a low-energy (LE) path with a 4 kV acceleration voltage. The HE path has a design identical to previous MC-ICP-MS models from Nu Instruments (*e.g.*, Nu Plasma 2), whereas the LE path is unique to the “Sapphire” model and it includes a hexapole collision/reaction cell that can remove Ar-related interferences. Software-controlled ion-beam deflectors are used to switch ion beams between HE and LE paths. Detailed descriptions on the design of “Sapphire” MC-ICP-MS are available in several recent studies.^{33,34,40}

An Apex Omega HF desolvating sample introduction system and a PFA Apex nebulizer with an uptake rate of 100 $\mu\text{L min}^{-1}$ (both from Elemental Scientific Inc., NE, USA) were used throughout this study. Because our collision/reaction cell was under the performance test during the early stage of this study, K isotope ratios were initially measured using the HE path and a “cold plasma” method. This method adopted a reduced radiofrequency (RF) power of 800 W and a high-mass-resolution source slit to yield a mass resolving power $> 10\,000$, allowing for $^{40}\text{Ar}^1\text{H}^+$ interferences to be partially resolved from $^{41}\text{K}^+$. Accurate $^{41}\text{K}/^{39}\text{K}$ ratio measurements, therefore, could be made on

the interference-free, low-mass side of K isotope peaks (*i.e.*, a pseudo-high-mass-resolution approach). The large Ar ion beam at mass 40 was not measured but absorbed by a “dummy bucket” to avoid ion scattering. A K concentration of $\sim 5 \mu\text{g mL}^{-1}$ was used during “cold plasma” measurements, typically yielding a voltage of 28 V for ^{39}K . Faraday cups equipped with $10^{11} \Omega$ resistors were used to simultaneously collect ^{39}K and ^{41}K in static mode. After all performance tests for the LE path were passed successfully, K isotope ratios were measured using the collision/reaction cell. High-purity (>99.999%) hydrogen and helium were used as collision/reaction gases, leading to removal of Ar and Ar-hydrides to a negligible level. Consequently, K isotopes were analyzed at a typical RF power of 1300 W and low-mass resolution with a resolving power of 300, which resulted in an ~ 200 -time increase in K sensitivity as compared to that obtained under “cold plasma” conditions. A considerably lower K concentration ($\sim 0.2 \mu\text{g mL}^{-1}$), therefore, was used during collision-cell measurements, typically yielding ~ 200 V for ^{39}K . A Faraday cup with a $10^{10} \Omega$ resistor was used to collect ^{39}K , whereas a Faraday cup with the default $10^{11} \Omega$ resistor was used to collect ^{41}K .

For both “cold plasma” and collision-cell measurements, the instrument was optimized for sensitivity and stability daily. Each measurement comprised 50 cycles of 5 s integration. A sample-standard bracketing protocol was used to correct for instrumental mass bias, and NIST SRM 3141a was used as the bracketing standard. Potassium concentrations in sample and bracketing standard solutions were matched within 5%. A concentration-mismatch correction was applied to all measured K isotope data based on a method we developed recently,³⁴ because this correction was found to be particularly critical to produce precise and accurate collision-cell measurements on a “Sapphire” MC-ICP-MS. The bracketing standard and purified samples were dissolved in 2% HNO_3 for the measurement. Background K intensity in blank 2% HNO_3 was measured before each measurement (“on-peak-zero”), and then subtracted from the intensity measured in the subsequent sample or bracketing standard measurement. The background K intensity was always <1% of the analyte intensity. In this study K isotope data are reported as δ -values in per mil (‰) on the NIST SRM 3141a scale:

$$\delta^{41}\text{K} = \left(\frac{{}^{41}\text{K}/{}^{39}\text{K}_{\text{sample}}}{{}^{41}\text{K}/{}^{39}\text{K}_{\text{NIST SRM 3141a}}} - 1 \right) \times 1000$$

Accuracy and precision of $^{41}\text{K}/^{39}\text{K}$ measurements were assessed by routine analysis of reference materials, including rock standards from the US Geological Survey and seawater, after normal sample preparation and chromatographic purification without the Na-TPB treatment. Our $\delta^{41}\text{K}$ results are compiled in ESI Table S2,[†] and no systematic bias was observed in $\delta^{41}\text{K}$ data measured by “cold plasma” and collision-cell methods. All results agreed well with those reported from other laboratories. Our long-term precision in $^{41}\text{K}/^{39}\text{K}$ is 0.08‰ (2SD) using the “cold plasma” method, and $\leq 0.05\text{‰}$ (2SD) using the collision/reaction cell. More technical details on K isotope analysis have been reported previously.³⁴

Potassium concentrations were measured by using a Thermo Scientific iCAP triple-quadrupole ICP-MS (TQ-ICP-MS) to quantify the K blank and yield. Sample solutions were introduced by a $100 \mu\text{g min}^{-1}$ nebulizer and a prepFAST autosampler. Potassium and sodium concentrations of some samples were analyzed on a Thermo iCAP 6000 series ICP-OES coupled with a CETAC ASX-520 autosampler to assess the effectiveness of matrix removal. During both ICP-MS and ICP optical emission spectrometry (ICP-OES) measurements, external calibration solutions were prepared by gravimetric dilution of high-purity Na and K single element standard solutions (High-Purity Standards, SC, USA), and yttrium (Y) was used as an internal standard during the measurement. The estimated precision for K and Na concentrations from both instruments was $\sim 5\%$ (1SD).

3. Results and discussion

3.1 K-TPB precipitation and Na-TPB salting-out

All TPB extraction experiments performed in this study were conducted at circumneutral pH in water, because it was observed in this study that acidic pH values caused low K yields due to either incomplete K-TPB precipitation or rapid decomposition of K-TPB precipitates. This does not prevent natural halite samples from being prepared by this extraction method because they are highly soluble in water. Extraction of K from test samples was conducted in 15 mL plastic centrifuge tubes. To initiate K-TPB precipitation, 0.35 mL 0.5 mol per L Na-TPB solution was introduced to a sample solution with an ionic strength of 2.5 mol L^{-1} (see Section 2.1.2). After addition of Na-TPB, the sample solution that was initially clear became increasingly cloudy, indicating the formation of K-TPB precipitates. The samples were left for ~ 3 hours (details in Section 3.3) before the K-TPB precipitates were separated from the solution and rinsed (details in Sections 3.4 and 3.5), followed by chromatographic purification (details in Section 3.6).

Initial tests were conducted at a higher ionic strength of 5 mol L^{-1} , but salting-out of Na-TPB salt was observed immediately after introduction of the precipitating solution to the sample, resulting in low K yields. Na-TPB salting-out was visually distinct from the formation of K-TPB precipitates; the former was characterized by immediate production of bright white precipitates in localized regions of the solution where the Na-TPB solution was introduced, whereas the latter was associated with comparatively gradual and uniform production of precipitates throughout the solution. Na-TPB solubility in pure water is 0.947 mol L^{-1} (K_{sp} : $8.97 \text{ mol}^2 \text{ L}^{-2}$) at 25°C .⁴⁷ Using this solubility data and eqn (5) that considers solution ionic strength, it can be calculated that the bulk solution should have remained under-saturated with respect to Na-TPB during TPB extraction at an ionic strength of 5 mol L^{-1} , contrary to laboratory observations. The observed Na-TPB salting-out was most likely to be caused by the high viscosity of the 5 mol per L NaCl solution that prevented effective solution mixing during addition of Na-TPB and, hence, led to local oversaturation of Na-TPB in the sample solution. Performing K extraction in solution at a lower ionic strength of 2.5 mol L^{-1} avoided the problem.

3.2 Potassium isotope fractionation during K-TPB precipitation

The magnitude of K isotope fractionation associated with K-TPB precipitation was not known previously, but this parameter is essential in evaluating the potential influence of incomplete K precipitation on $\delta^{41}\text{K}$ values measured for the samples. In addition, there is strong interest in applying stable K isotopes to study the K nutrient cycle in the soil–plant system,^{50,51} and Na-TPB has been commonly used in soil and agronomy sciences to extract exchangeable (or plant-available) K from soils for K concentration measurements,^{51,52} so it is almost certain that the need for K isotope analyses of TPB-extracts from soils and/or clay minerals will soon emerge in relevant research. Potassium isotope fractionation during K-TPB precipitation will then be a useful parameter needed to interpret $\delta^{41}\text{K}$ data from TPB-extracts in future studies.

Partial precipitation experiments were conducted to quantify K isotope fractionation during K-TPB precipitation. Parallel reactors, each of which contained 5 mL K solution with a total of 500 μg K sourced from UMN-K, were set up. Different amounts of the 0.5 mol per L Na-TPB solution were added into different reactors to induce K-TPB precipitation of varying extents. The use of a relatively large K mass in these experiments was intended to ensure sufficient K masses in both precipitates and remaining solutions for high-precision K isotope ratio measurement. Precipitates and the remaining solutions were separated after the reaction by filtration, following the protocol provided in Section 3.7. Small aliquots were taken from the initial solution and aqueous samples after the TPB reaction for K concentration measurements on iCAP TQ-ICP-MS so that the extent of K precipitation in each reactor could be quantified. The remaining aqueous samples and their associated K-TPB precipitates were then purified chromatographically, followed by measurement of their K isotope ratios by MC-ICP-MS.

The measured $\delta^{41}\text{K}$ values for K-TPB precipitates and their associated K solutions are plotted as a function of the fraction of K

remaining in solution (Fig. 3). Based on aqueous K concentration results, 23% to 100% K was precipitated from the initial solution. K-TPB precipitates produced by partial precipitation were isotopically lighter than the initial solution (Fig. 3), demonstrating preferential incorporation of light K isotopes into K-TPB solids. The process was not consistent with steady-state K isotope fractionation but could be explained by a Rayleigh distillation process, with a best-fit K isotope fractionation factor of -0.65‰ in $^{41}\text{K}/^{39}\text{K}$ between K-TPB solids and aqueous K (Fig. 3). The results indicate that incomplete K precipitation during the extraction procedure can cause a biased $\delta^{41}\text{K}$ value that is lower than the true value of a sample, highlighting the importance of quantitative recovery of K during the TPB extraction procedure. Based on the estimated K isotope fractionation factor, when the degree of K-TPB precipitation is <98% of the total K in a sample, the $\delta^{41}\text{K}$ bias would become resolvable by K isotope ratio measurement with state-of-the-art precision (*i.e.*, 0.05‰ , 2SD).

3.3 Optimization of the TPB reaction duration

It is critical to optimize the duration allowed for Na-TPB to react with the sample solution before K-TPB precipitates are separated from the aqueous phase. A duration that is too short may result in incomplete reaction of K with Na-TPB and, hence, a compromised recovery of K from a sample. A duration that is too long not only unnecessarily lengthens the sample preparation process, but also may run the risk of TPB degradation that leads to release of K from the insoluble K-TPB precipitates back to the solution. Previous studies have shown that both Na- and K-TPB salts can decompose in aqueous solution,^{53–55} but these studies were often conducted under conditions different from those relevant to the K extraction method developed here. It is, therefore, unknown if TPB decomposition could affect K extraction in this new method.

A series of test samples that each contained 50 μg K sourced from the in-house UMN-K standard were reacted with the same amount of 0.5 mol per L Na-TPB for different durations ranging from 5 minutes to up to 24 hours. The resulting K-TPB precipitates from all the test samples were recovered, rinsed, and purified using the protocol provided in Section 3.7, followed by K isotope analysis. The test for each reaction duration was conducted in triplicate.

The test results are summarized in Fig. 4. Although white K-TPB precipitates appeared as soon as the Na-TPB precipitating solution was introduced into sample solutions in all experiments, the 5 min reaction experiment yielded $\delta^{41}\text{K}$ values consistently lower than the true value, indicating insufficient time for the TPB reaction (hence K extraction) to proceed to completion. The 3 hour reaction experiment produced the most accurate and precise $\delta^{41}\text{K}$ results compared to other tests performed in this study. With increasing reaction time (*i.e.*, 17 and 24 hours), $\delta^{41}\text{K}$ results gradually became lower than the true value, and the $\delta^{41}\text{K}$ reproducibility based on the triplicate tests also worsened. This trend can be explained by degradation of K-TPB or TPB ions that led to progressively lower and less consistent K yields with time. According to these results, a ~ 3 hour reaction time is adopted in the extraction procedure.

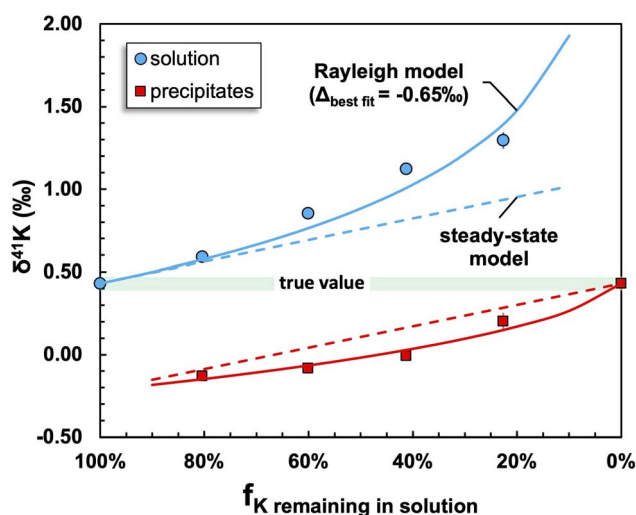


Fig. 3 Quantification of the K isotope fractionation factor associated with K-TPB precipitation.

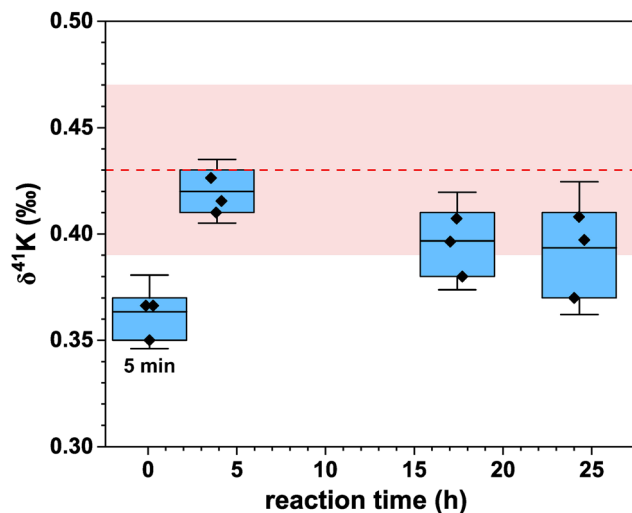


Fig. 4 K isotope results from the experiments intended to establish the optimal reaction time for K-TPB precipitation.

3.4 Separation and recovery of K-TPB precipitates

It is mandatory to separate K-TPB precipitates from the associated Na-rich solution to effectively reduce the Na level in the processed samples, but separation and quantitative recovery of K-TPB were challenging because K-TPB precipitates were typically finely dispersed in the solution and centrifugation was found to be ineffective in achieving complete separation of K-TPB from the solution.

An effective and convenient two-stage filtration protocol was developed to quantitatively recover K-TPB precipitates from solution, using disposable syringe filters with closed filter housing. During the first stage, sample slurries were shaken well and then poured into pre-cleaned disposable syringes with filters. The filtrate was discarded, whereas insoluble K-TPB solids were retained on the filter membrane enclosed in filter housing. Once the first-stage separation was complete, K-TPB solids in filter housing were recovered by a second-stage filtration that slowly pushed Optima-grade acetone through the filter. Because the solubility of K-TPB in acetone at room temperature is more than 2 orders of magnitude higher than its solubility in water,⁴⁷ the K-TPB precipitates were dissolved nearly instantly as acetone was passed through the filter. The K-bearing acetone filtrate was collected in a Teflon beaker. To maximize K recovery, the acetone solution was first added into the sample reactor to rinse off and dissolve any K-TPB residues in the reactor. This acetone solution was then poured from the sample reactor into the same syringe used in the first-stage filtration and then slowly pushed through the filter. This operation was typically repeated 3 times using a total of 5 mL acetone (2 mL, 2 mL, and 1 mL), and K-TPB precipitates were quantitatively recovered in this 5 mL acetone. In the final optimized protocol, a rinsing step was added between the first and second filtration steps to further reduce Na in the recovered K-TPB precipitates (details in Section 3.5).

Four different types of syringe filters purchased from VWR International were tested to determine the best filter type for the

K-TPB recovery protocol, including 13 mm-diameter filters with 0.2 μm (part no.: 28145-491) and 0.45 μm pore sizes (part no.: 28145-493), and 25 mm-diameter filters with 0.2 μm (part no.: 28145-495) and 0.45 μm pore sizes (part no.: 28145-497). All filters tested had a PTFE membrane and polypropylene housing. A series of test samples that contained 20 μg K each were precipitated by Na-TPB, and the resulting K-TPB precipitates were then separated and recovered by using different filters following the protocol described above. Potassium concentrations of the solutions recovered from all the experiments were analyzed on an iCAP TQ-ICP-MS, which allowed for calculation of K yield for each experiment. All sample preparation and treatments were performed in the same fashion to ensure that any difference in the results could be directly attributed to the filter type.

The results showed that 0.2 μm filters typically provided higher K yields as compared to 0.45 μm filters of the same diameter (Fig. 5), implying that some fine K-TBP precipitates can escape filters with a larger pore size. When filters with the same pore size were considered, the smaller diameter 13 mm filters provided perceptibly higher K yields compared to that obtained using the larger 25 mm filters (Fig. 5). This difference may be caused by larger dead volume in filter housing of a larger diameter, which can impede effective recovery of K-TPB precipitates by acetone. As a result, 13 mm-diameter syringe filters with a 0.2 μm pore size were adopted in the procedure.

3.5 Rinsing of K-TPB precipitates

It is essential to further reduce the Na level in K-TPB precipitates separated from the associated Na-rich solution because a considerable amount of Na can be adsorbed on K-TPB solid surfaces or present in the interstitial space of K-TPB solids. Washing experiments were performed to determine an effective rinse protocol that can further reduce Na in post-extraction K-TPB precipitates without causing K loss. A series of test samples (*i.e.*, 20 μg K in 1 g NaCl) were processed using Na-TPB.

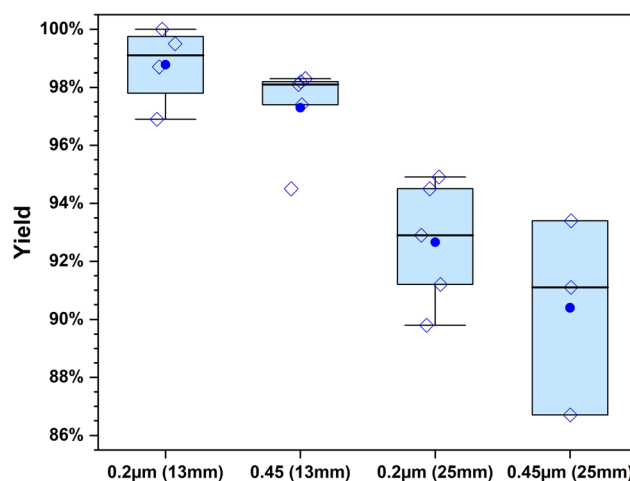


Fig. 5 Results of K-TPB recovery by different filters. Open diamonds denote measured values, and blue filled circles represent experiment averages for each filter type.

Resultant K-TPB precipitates were separated from the solution by using syringe filters and then rinsed on the filter by using different solutions. Rinse solution was added by using a pipettor into the same syringe used to separate K-TPB and then slowly pushed through the same filter that contained K-TPB solids. Three rinse solutions were tested, including pure H₂O, 0.05 mol per L Na-TPB, and 0.1 mol per L Na-TPB. The number of washes, ranging from no wash to 5 times, was also tested for each rinse solution, with each wash using 1 mL rinse solution. K-TPB precipitates were recovered from filters using acetone, followed by analyses of their Na/K ratios by ICP-OES.

The results show that K-TPB precipitates recovered without any wash had Na/K mole ratios of ~ 240 (Fig. 6), which already represented a >2 -order-of-magnitude reduction in Na relative to the initial Na/K mole ratio of $\sim 3.3 \times 10^4$ in the “halite” test samples. However, Na levels were still too high to be adequately purified by the existing two-stage column separation for accurate K isotope ratio measurement;³⁴ erroneous $\delta^{41}\text{K}$ results were obtained on a Sapphire MC-ICP-MS when K-TPB precipitates were directly purified without any wash.

All three rinse solutions were able to further reduce Na in K-TPB precipitates (Fig. 6). Washing with H₂O yielded the lowest Na/K ratio after 2 rinses, but it caused significant dissolution of K-TPB precipitates (and hence K loss). Although K-TPB has very

low solubility in water, the volume of water used during rinsing was comparably large relative to the small quantity of K-TPB precipitates resulting from the extraction. This could shift the K-TPB solubility equilibrium towards dissolution, leading to significant loss of K. In contrast, neither 0.05 nor 0.1 mol per L Na-TPB solution caused measurable K loss after at least up to 4 rinses, because the presence of TPB[−] anions in the rinse solution could effectively prevent dissolution of K-TPB solids. Na/K ratios of K-TPB solids remained relatively steady after the first rinse using either of the two Na-TPB solutions, but the plateau Na/K ratio obtained using 0.05 mol per L Na-TPB as the rinse solution was $\sim 50\%$ lower than the ratio achieved using 0.1 mol per L Na-TPB. This difference implies that the final level of Na remaining in K-TPB precipitates was primarily controlled by the rinse solution trapped in the dead space of the filter housing. Based on these test results, 0.05 mol per L Na-TPB was adopted to rinse K-TPB precipitates, and 3 rinses using 1 mL rinse solution each time were performed routinely to ensure consistent removal of Na to the maximum level possible. This rinse protocol reduced Na in post-extraction K-TPB precipitates to a Na/K level comparable to that of natural seawater (Fig. 6), which could be easily purified by any published column separation method for high-precision stable K isotope measurement.³⁴

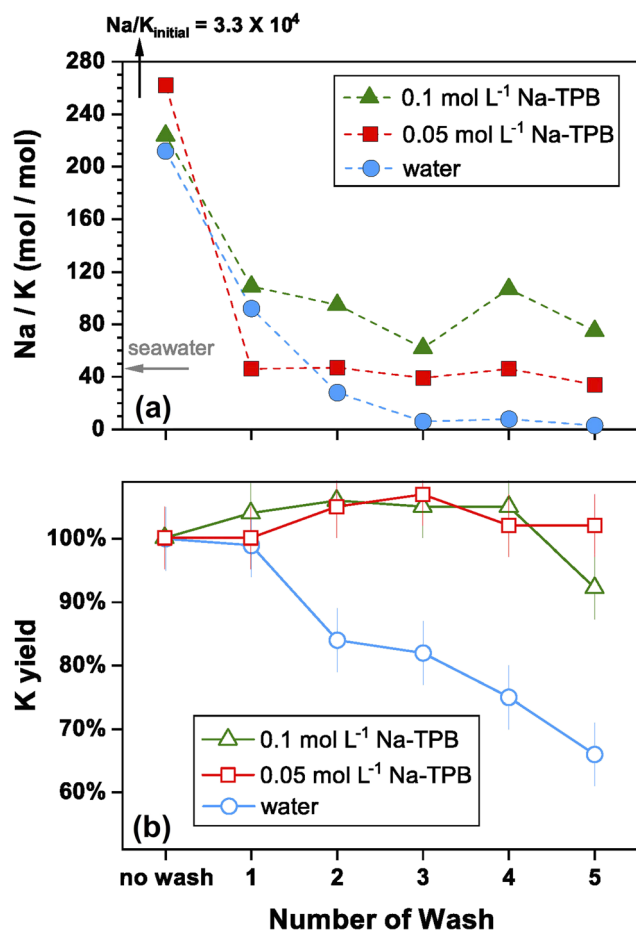


Fig. 6 Effects of different rinse types and volumes on Na removal (a) and K yield (b).

3.6 Removal of TPB anions

It is essential to purify K from sample matrices to ensure precise and accurate K isotope analysis by MC-ICP-MS,³⁴ but chromatographic purification of the TPB-extraction products is hampered by the low solubility of K-TPB precipitates in water and common mineral acids. Because TPB salts are unstable and can degrade into a series of organic compounds (e.g., benzene and phenol) at acidic pH values and elevated temperatures,^{53,56} attempts were made to decompose K-TPB solids by using concentrated acids (HCl, HNO₃, or aqua regia) at 120 °C for a few days. The occurrence of significant TPB degradation was indicated by the change of solution color into brownish, but considerable solid residues remained after the treatment and none of the acids tested were able to completely dissolve the solids.

This difficulty was solved by removal of TPB[−] anions from K⁺ using a chromatographic separation approach. Design of this approach took advantage of the high solubility of K-TPB and its possible organic degradation products in acetone.⁴⁷ 5 mL acetone used to recover all K-TPB from the precipitation procedure was first acidified to 0.2 mol per L HCl to keep K in its ionic form dissociated from the TPB complex, and the acidified acetone solution was then directly loaded onto a Bio-Rad chromatographic column filled with 2 mL AG50W-X8 (H⁺ form, 200–400 mesh) cation exchange resin. This is the same column used in my laboratory to purify K for high-precision stable K isotope analysis.³⁴ Potassium cations were quantitatively retained on AG50W-X8 resin, whereas TPB[−] anions (and other anionic/molecular degradation products) were eluted using a 0.2 mol per L HCl and 70% (v/v) acetone mixture. To establish the volume of wash needed to remove all TPB[−] anions,

the eluate was collected as separate 1 mL increments until a total of 15 mL HCl-acetone mixture was passed through the column. All 1 mL cuts were then evaporated to complete dryness on a hotplate and inspected visually. Because of the large molar weight of the TPB[−] anion (*i.e.*, 319), solid residues could be easily seen at the bottom of beakers after evaporation when even only a small amount of TPB[−] was present. It was observed that visible residues disappeared after the first 2 mL HCl-acetone mixture, consistent with the expectation that TPB[−] should not be adsorbed by the cation-exchange resin. In this study, a larger volume (*i.e.*, 7 mL) of the HCl-acetone mixture was used to ensure complete removal of TPB[−] anions from the samples.

This chromatographic approach for TPB[−] removal has several advantages. First, K-TPB precipitates recovered in acetone from the TPB-extraction procedure can be conveniently processed through the chromatographic column without any need for prior sample evaporation or redissolution. This improves the sample throughput significantly. Second, the TPB[−] removal step can be directly followed by chromatographic purification of K due to the use of the same column. Importantly, because of the low HCl molarity (0.2 mol L^{−1}) in the HCl-acetone mixture, the TPB[−] elution step was found to have little effect on eluting K from the chromatographic column. As a result, the original K elution protocol reported in Zheng *et al.* (2022)³⁴ was found to be still valid, and no additional work was required to re-calibrate the K elution protocol after TPB[−] removal. Once K was recovered from the entire chromatographic separation procedure, it was found that the resulting K salts could be easily dissolved in water or weak acid (*e.g.*, 2% HNO₃), indicative of successful removal of TPB[−]. The samples are then ready for K isotope analysis by MC-ICP-MS.

3.7 The recommended K extraction procedure and method validation

Based on all the test results reported above, a fully optimized TPB-based K extraction procedure is summarized in Table 1. The total procedure blank that includes both K extraction and

subsequent chromatographic separation was measured to be ~100 ng K. The contributions of various sources to this total procedural blank were quantified. It was measured that 5 mL Optima-grade acetone contained 11.5 ± 5.4 ng K (1SD, *n* = 4), representing ~12% of the total procedural blank. The K blank in 0.35 mL of the 0.5 mol per L Na-TPB solution was measured to be 4.1 ± 0.1 ng K (1SD, *n* = 2), representing ~4% of the total procedural blank. Column separation, including step 6 and step 7 in Table 1, introduced 11.6 ± 1.7 ng K (1SD, *n* = 2), accounting for ~12% of the total procedural blank. The K blank introduced by the filtration step was assessed by processing 0.35 mL of the 0.5 mol per L Na-TPB solution as a test sample according to steps 3 and 4 in Table 1. The potential K blank on the filter was recovered in 5 mL acetone and measured. The measured K levels were indistinguishable from those measured in 5 mL of acetone without filtration, indicating negligible K introduced by the filtration step. The majority of the total procedural blank (~73 ng K) originated from the 1 g NaCl matrix used to make the synthetic “halite” test sample. When applying this new extraction method to natural samples, the total procedural blank level will be ~27 ng K because the K blank from NaCl is avoided. As shown below, this procedure can extract as little as 20 µg K from solutions with extremely high levels of Na (up to a 1 g NaCl matrix). The K-TPB precipitation in laboratory conformed to the theoretical calculations presented in Section 2.1.2, thereby demonstrating that the procedure is grounded in a good understanding of the fundamental chemistry involved.

The new procedure was validated using synthetic halite samples doped with K with a known K isotope composition, because of the absence of an appropriate certified material or natural halite samples that were previously measured for stable K isotopes. Aliquots of the synthetic halite solution, each containing 1 g of dissolved NaCl, were taken and doped with 100 µg, 50 µg, and 20 µg K sourced from UMN-K. Although the total procedural blank (~100 ng) is not trivial, especially for the 20 µg K “halite” test sample where the blank would account for ~0.5% of the total K, it should have negligible influence on the measured $\delta^{41}\text{K}$ values of all “halite” test samples. This can be understood through the following two-component mixing calculation, where the measured $\delta^{41}\text{K}$ in the test sample ($\delta^{41}\text{K}_{\text{measured}}$) reflects the mixing of K from the blank ($\delta^{41}\text{K}_{\text{blank}}$) and from the actual sample ($\delta^{41}\text{K}_{\text{true}}$):

$$\delta^{41}\text{K}_{\text{measured}} = (1 - f) \times \delta^{41}\text{K}_{\text{true}} + f \times \delta^{41}\text{K}_{\text{blank}}$$

Here, *f* is the fraction of K from the blank in the total sample, which is ~0.5% in the 20 µg K “halite” test sample. For the influence of this level of the K blank on the measured $\delta^{41}\text{K}$ of this test sample to be measurable with state-of-the-art analytical precision (*i.e.*, $|\delta^{41}\text{K}_{\text{measured}} - \delta^{41}\text{K}_{\text{true}}| \geq 0.05\text{‰}$), the blank would need to have a very extreme $\delta^{41}\text{K}$ value, either $\geq 10.48\text{‰}$ or $\leq -9.62\text{‰}$. Such extreme $\delta^{41}\text{K}$ values have not been observed on Earth, making it very unlikely that the K blank could significantly influence even the measured $\delta^{41}\text{K}$ value of the 20 µg K test sample beyond current analytical uncertainty. The samples were processed according to the procedure described in Table 1, and then analyzed on a Sapphire MC-ICP-MS.

Table 1 The recommended K extraction procedure based on TPB chemistry

Step 1	Dissolving the sample in Milli-Q water to make a solution with an ionic strength of 2.5 mol L ^{−1}
Step 2	Adding 0.35 mL 0.5 mol L ^{−1} Na-TPB to the sample solution and waiting for 3 hours
Step 3	Separating K-TPB precipitates by using a 13 mm 0.2 µm PTFE membrane syringe filter
Step 4	Washing K-TPB on the filter with 3 mL 0.05 mol L ^{−1} Na-TPB (1 mL rinse × 3 times)
Step 5	Recovering K-TPB from the filter using 5 mL acetone (2 mL, 2 mL, and 1 mL)
Step 6	Loading the acidified acetone solution (to 0.2 mol L ^{−1} HCl) onto a Bio-Rad column filled with 2 mL AG50W-X8 (200–400 mesh) resin and eluting TPB ions by using 7 mL of a 0.2 mol L ^{−1} HCl + 70% (v/v) acetone mixture
Step 7	Purifying and recovering K using the existing elution protocol reported in Zheng <i>et al.</i> (2022) ³⁴

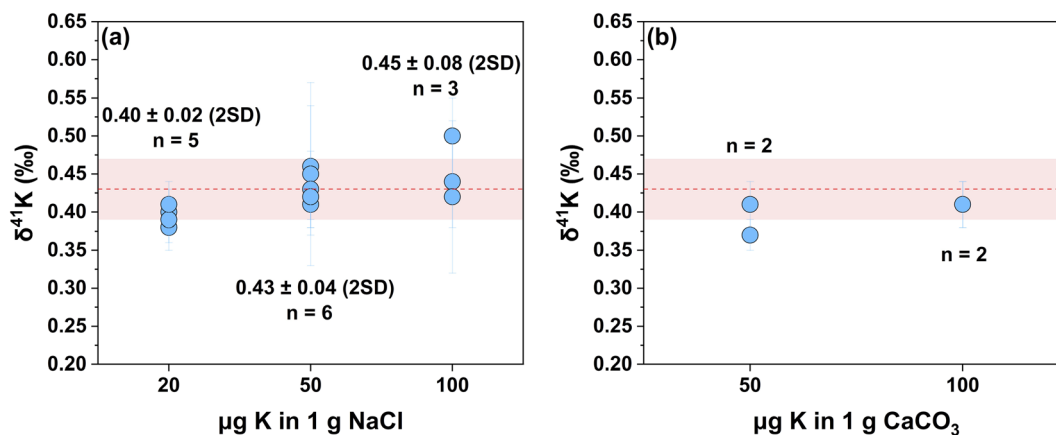


Fig. 7 K isotope results for "halite" (NaCl) test samples (a) and "carbonate" (CaCl_2) test samples (b). Note that the "carbonate" test samples were in a CaCl_2 matrix, and "1 g CaCO_3 " refers to the equivalent amount of CaCl_2 produced by fully dissolving 1 g CaCO_3 in HCl.

Accurate and precise $\delta^{41}\text{K}$ results were obtained for all the test samples (Fig. 7a), showing the effectiveness of the new K extraction procedure developed here.

3.8 Possible extension of the procedure to carbonate samples

Carbonates represent another important sample type pertinent to K isotope research,^{21,22} but they also have low K concentrations, typically 100 $\mu\text{g g}^{-1}$ or less, making it challenging to separate K from high calcium matrices for high-precision stable K isotope analysis. Taking advantage of the high K sensitivity offered by the latest collision-cell MC-ICP-MS, a recent study developed an optimized chromatographic procedure that could prepare carbonate samples for K isotope analysis.⁴¹ However, the maximum mass of bulk carbonates that can be processed by this chromatographic procedure is limited to ~ 100 – 150 mg,⁴¹ dictated by the resin cation-exchange capacity. This means that the quantity of K purified by this procedure is small and analysis of the sample is likely restricted to laboratories having access to collision-cell MC-ICP-MS instruments with high K sensitivity.

Although it is not the focus of this study, a few experiments were conducted to explore possible applications of the new TPB-based K extraction procedure to carbonates. Aliquots of the synthetic "carbonate" solution, each containing the amount of dissolved CaCl_2 equivalent to dissolution of 1 g CaCO_3 , were taken and doped with 100 μg and 50 μg K sourced from UMN-K. The samples were processed according to the procedure described in Table 1, and then analyzed on a Sapphire MC-ICP-MS. One caveat is that activities of different ions (K^+ , Ca^{2+} , and TPB^-) in a Ca–K–TPB system at elevated ionic strengths are not well constrained, so the current application relies on the knowledge for a Na–K–TPB system (eqn (5)). Nonetheless, accurate $\delta^{41}\text{K}$ results were obtained for all the test samples (Fig. 7b), indicating similar behaviors of a Ca–K–TPB system and a Na–K–TPB system. These preliminary results show that the TPB extraction method developed primarily for Na-rich samples has great potential for providing a simple alternative for

preparing carbonate samples for K isotope analysis. Further studies that constrain activities of different ions (K^+ , Ca^{2+} , and TPB^-) in a solution at a wide range of ionic strengths are warranted and could provide useful guidance on more precise control of TPB precipitation in a Ca-rich matrix. Because the TPB-based extraction method can process large bulk carbonate samples (e.g., 1 gram), ~ 7 to 10 times larger than that can be processed by the latest chromatographic method,⁴¹ it is possible to purify a considerably larger K mass for isotope analysis using this method. Consequently, this method can facilitate K isotope research on carbonates in laboratories without access to the latest collision-cell MC-ICP-MS instruments.

4. Conclusions

This study presents a novel and efficient K extraction procedure based on tetraphenylborate (TPB) chemistry. Development of this procedure was guided by an in-depth understanding of chemical stoichiometry of the TPB reaction and solubility equilibrium of relevant TPB salts. The potassium isotope fractionation factor associated with K–TPB precipitation was experimentally determined to be -0.65‰ , with light K isotopes being preferentially incorporated into K–TPB solids. This isotope fractionation highlights the importance of quantitative K extraction for accurate K isotope measurements. Experiments were conducted to optimize several key parameters of this procedure, including the TPB reaction time, K–TPB solid recovery and rinses, and removal of TPB anions. This procedure allows for (near-)quantitative extraction of K from large quantities of bulk samples that have low K concentrations but extremely high Na (and Ca) matrices. The procedure is efficient and can be completed within only a couple of hours. After being treated by this extraction procedure, the samples that are conventionally difficult, if not impossible, to purify can be successfully processed by the existing chromatographic separation methods for high-precision stable K isotope analysis. The primary sample type targeted by this study is halite (NaCl), and this new procedure enables study of the K isotope composition in fluid inclusions in marine halite. This technique can advance

research into reconstructing $\delta^{41}\text{K}$ variations in ancient oceans and, hence, unraveling the intricate influence of silicate weathering and authigenic clay formation on Earth's long-term climate dynamics. It is also shown here that this new procedure can be extended to process carbonates, another type of sample pertinent to K isotope research but challenging to analyze due to their low K concentrations and high Ca matrices.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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