Ab Initio Calculation of Equilibrium Isotopic Fractionations of Potassium and Rubidium in Minerals and Water

Hao Zeng,†‡ Viktor F. Rozsa,† Nicole Xike Nie,† Zhe Zhang,† Tuan Anh Pham,§ Giulia Galli,§∥⊥ and Nicolas Dauphas‡∥⊥

†Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, and ‡Pritzker School of Molecular Engineering, The University of Chicago, Chicago, Illinois 60637, United States
§Quantum Simulations Group, Lawrence Livermore National Laboratory, Livermore, California 94551, United States
∥Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States
⊥Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States

ABSTRACT: We used first-principle approaches to calculate the equilibrium isotopic fractionation factors of potassium (K) and rubidium (Rb) in a variety of minerals of geological relevance (orthoclase, albite, muscovite, illite, sylvite, and phlogopite). We also used molecular dynamics simulations to calculate the equilibrium isotopic fractionation factors of K in water. Our results indicate that K and Rb form bonds of similar strengths and that the ratio between the equilibrium fractionations of K and Rb is approximately 3−4. Under low-temperature conditions relevant to weathering of continents or alteration of seafloor basalts (∼25 °C), the K isotopic fractionation between solvated K+ and illite (a proxy for K-bearing clays) is +0.24‰, exceeding the current analytical precision, so equilibrium isotopic fractionation can induce measurable isotopic fractionations for this system at low temperature. These findings, however, cannot easily explain why the δ41K value of seawater is shifted by +0.6‰ relative to igneous rocks. Our results indicate that part of the observed fractionation is most likely due to kinetic effects. The narrow range of mean force constants for K and Rb in silicate minerals suggests that phase equilibrium is unlikely to create large K and Rb isotopic fractionations at magmatic temperatures (at least in silicate systems). Kinetic effects associated with diffusion can, however, produce large K and Rb isotopic fractionations in igneous rocks.

KEYWORDS: isotopes, equilibrium fractionation, concentration effect, potassium, rubidium

1. INTRODUCTION

Potassium is a moderately volatile, lithophile element that is present in relatively high abundance in the ocean (eighth most concentrated element),1 Earth’s crust (eighth),1−3 bulk silicate Earth (BSE; seventeenth),4,5 and in the solar system (twentieth).6−8 The limited precision achievable by mass spectrometry in measuring the ratios of the isotopic abundances of 39K, 40K, and 41K has long limited the application of K isotope systematics to cosmochemistry, where large isotopic variations have been found.9−16 Thanks to improvements in purification protocols and multicolonlector inductively coupled plasma mass spectrometry (MC-ICPMS), the isotopic composition of K (expressed using the 41K/39K ratio) can now be measured with a precision of ∼0.1‰,17−24 spurring wide interest in K isotopes, which have now been used to study weathering,21,25 seafloor alteration,23 and volatile element depletion in planetary materials.10,12,15,17 Potassium isotopic compositions are reported as the per mil (‰) deviation (δK) of the ratio of two potassium stable isotopes 41K (6.730%) and 39K (93.258%), relative to the inferred composition of the mantle or the NIST standard reference material 3141a. Because of direct isobaric interferences from 40Ar+ and 40Ca+ on 40K+ in MC-ICPMS and the low abundance of 40K (0.012%), the latter isotope is often not reported. This is inconsequential because K isotopic variations are thought to follow the laws of mass-dependent fractionation, meaning that the relative deviations in the 40K/39K ratio are approximately half those of the 41K/39K ratio (δ41K = 2 δ40K).26,27 Also belonging to the alkali group, Rb shares similar chemical and physical properties with K and substitutes for K in minerals such as feldspar. As a result, the K/Rb weight (g/g) ratio varies little both among meteorites28 and within various geochemical reservoirs in the Earth (400 for the BSE; 232 for the crust).1−5 Notable exceptions to the constancy in the K/Rb weight ratio are rivers (∼1000)29 and seawater (∼3765).30 The elevated K/Rb ratio of seawater compared to that of the BSE could be due to the preferential mobilization of K relative to Rb during continental weathering30 as well as the preferential uptake of Rb relative to K during seafloor
Rubidium isotopic ratios can be measured with great precision, but the similarity in the geochemical behaviors of K and Rb raises the question of whether measuring the isotopic compositions of K and Rb on the same samples provides additional insight compared to measuring K or Rb alone.

Understanding how K and Rb isotopes are fractionated at equilibrium between vapor and condensed phases is important to use these systems for understanding why planetary bodies are depleted in these moderately volatile elements. It has been shown that lunar rocks are enriched in the heavy isotopes of K by ~0.4‰, which was interpreted by Wang and Jacobsen to reflect equilibrium isotopic fractionation between liquid and vapor under conditions relevant to the Moon-forming giant impact event. Nie and Dauphas et al. contended that at the temperature of ~3500 K, most likely relevant to Moon formation, the equilibrium fractionation between vapor and condensate would be too small, implying the involvement of kinetic isotopic fractionation presumably associated with vaporization. Similarly, lunar rocks are enriched in heavy Rb isotope relative to terrestrial rocks and those data are consistent with a scenario that involves loss of volatile elements from the protolunar disk by accretion onto the Earth, leaving behind a Moon that is depleted in moderately volatile elements.

Water–mineral interactions play a significant role in maintaining habitable conditions at the surface of the Earth through silicate weathering and carbonate precipitation. The isotopic compositions of K and Rb could help trace continental weathering and reverse weathering in marine sediments, which both influence climate through their controls of CO₂ partial pressure in the atmosphere (and associate greenhouse effect). Li et al. found that the ocean is significantly enriched in the heavy isotopes of K relative to the BSE by δ¹⁴K_{ocean–BSE} ≈ +0.6‰ and the cause of this enrichment remains unclear. As summarized by Santiago-Ramos et al., this enrichment could arise from the removal of K from the oceans involving authigenic Al-silicate formation in marine sediments and/or low-temperature alteration of the oceanic crust. Alternatively, the enrichment could originate from isotopic fractionation during mobilization of K associated with continental silicate weathering or high-temperature basalt alteration. Santiago-Ramos et al. studied K isotopic fractionation in sediment pore-fluids and concluded that K removal in authigenic Al-silicates in sediments could be responsible for such fractionation as pore-fluids tend to be enriched in the light isotopes of K. The driver for this fractionation could be diffusion through the porewater, which is kinetic in origin. Equilibrium fractionation between K⁺ dissolved in porewater and K incorporated in minerals could also play a role but the extent of this fractionation is unknown. Characterizing equilibrium isotopic fractionation between aqueous fluids and K-bearing silicates is also important for understanding how K isotopes are fractionated during weathering.

Despite progress made in measuring the isotopic compositions of K and Rb, understanding the cause of the isotopic variations for those elements in natural systems can be challenging, partly due to an insufficient theoretical understanding of how equilibrium and kinetic processes control the fractionations of K and Rb isotopes. To address this, Li, Y. et al. recently calculated the reduced partition function ratio (rpfr) of K in alkali feldspar and studied the concentration effect on K fractionation using density functional theory (DFT). Additionally, Li, W. et al. studied experimentally equilibrium fractionation between K dissolved in water and K salts such as halides, sulfates, and carbonates. They also performed ab initio calculations for the salts that they studied. Clearly, more work is needed to understand how the isotopic compositions of Rb and K are fractionated at equilibrium between different minerals, gaseous species, and water. These fractionations are critical for interpreting the origin of K isotopic variations in low-temperature aqueous systems and planetary/nebular processes that involved the volatilization of K and Rb.

Understanding the isotopic fractionation of K between water and K-bearing minerals requires knowledge of the speciation of K in water. As ~99% of aqueous K in the oceans is present as hydrated K⁺, we chose to focus on hydrated K⁺ in this study. In contrast to other cations, in particular divalent ones (e.g., Zn²⁺), the hydration shell of K⁺ is not as well defined, with water molecules rapidly exchanging within the first solvation shell. Because equilibrium fractionation properties are highly sensitive to coordination numbers and to nearest neighbor distances, we used first-principle molecular dynamics (FPMD) to study hydrated K⁺, capturing many instantaneous configurations of the fully hydrated K⁺, in contrast to a cluster approach where static hydrated configurations are considered.

Our results suggest that (a) equilibrium fractionation between K-bearing clays (illite) and seawater could be a significant source of oceanic K enrichment and (b) the bond strengths of Rb and K are similar, so equilibrium processes are expected to impart correlated isotopic fractionations to Rb and K that differ from kinetic processes, providing a means of distinguishing between equilibrium and kinetic processes in nature.

2. METHOD

2.1. Equilibrium Fractionation. Equilibrium isotope fractionation for an element X between two phases A and B (α_{A→B}) can be calculated using the rpfr (or β-factor) of each phase:

$$\alpha_{A→B} = \frac{(X'/X)_A}{(X'/X)_B} = \frac{\beta_A}{\beta_B}$$

where X, X’ refer to the abundances of two isotopes of an element. The rpfr can be calculated from:

$$\beta = \left( \prod_{i=1}^{N} \prod_{q} \frac{v_{i}'}{v_{i}} e^{-\Delta_{i}/2kT} \frac{1 - e^{-\Delta_{i}/kT}}{1 - e^{-\Delta_{i}/kT}} \right)^{1/N}$$

where N is the total number of atoms in the unit cell, v_{i}/v_{i}' are the frequencies of vibrational mode i for two isotopes at a given wavevector q. N_q is the total number of q-vectors, and n is the number of isotopic sites in the unit cell. When measured experimentally, equilibrium isotopic fractionation (in %) between two phases is expressed as:

$$\Delta_{A→B} (\%) = 1000 \ln \alpha_{A→B} = 1000 (\ln \beta_A - \ln \beta_B)$$

To a good approximation, one can write 1000 ln β as a polynomial expansion in even powers of the inverse of the temperature.
1000 \ln \beta = \frac{A_1}{T} + \frac{A_2}{T^2} + \frac{A_3}{T^3}

(4)

where \( A_1, A_2, \) and \( A_3 \) are constants that depend on the mineral/phase considered. The coefficient of the first-order term, which always dominates the rpf, especially at high temperature (>200 K), can be rewritten as

\[ A_1 = 1000 \left( \frac{1}{M} - \frac{1}{M'} \right) \frac{h^2}{8k^2} \]

(5)

where \( h \) is the reduced Planck constant, \( k \) is Boltzmann’s constant, \( M' \) and \( M \) are the masses of the two isotopes, and \( (F) \) is the mean force constant of the K or Rb bonds (equivalent to the spring constant of a harmonic spring), which can be calculated from the partial phonon density of states (PDOS, \( g(E) \))

\[ F = \frac{M}{\hbar^2} \int_0^{\infty} E^2 g(E) dE \]

(6)

At high temperature for \(^{39/41}\text{K} \) and \(^{85/87}\text{Rb} \), eq 4 can be written as

\[ 1000 \ln \beta_k \approx 5500 \frac{(F)}{T^2} \]

(7)

\[ 1000 \ln \beta_{\text{Rb}} \approx 1189 \frac{(F)}{T^2} \]

(8)

At low temperature relevant to weathering, for example, the full expansion in eq 4 should be used.

2.2. FPMD of the Potassium Ion in Water. We carried out FPMD of aqueous K⁺ using the Perdew, Burke, and Ernzerhof (PBE) exchange–correlation functional.\(^{54} \) This relatively simple functional was chosen as it was reported that there is no significant difference in rpf calculated from PBE and van der Waals functionals.\(^{39} \) We used the same functional for minerals and hydrated potassium, to facilitate comparing frictionation factors for different systems and to take advantage of cancellation of errors.

We performed Born–Oppenheimer molecular dynamics (BOMD) simulations with the Qbox code.\(^{55} \) We used a cubic cell containing 63 water molecules and one K⁺ and a volume chosen so as to obtain the measured density of water at ambient conditions (edge length equal to 12.4 Å). A compensating uniform background charge was used to ensure charge neutrality. All hydrogen atoms were replaced with deuterium to allow for a larger timestep, chosen to be 10 fs. The 3s and 3p semicore states of K were treated with LDA pseudopotentials from the GBRV library and Quantum ESPRESSO PSlibrary (PSL).\(^{66} \) Pseudopotentials from PSL used in this study include Na.pz-n-vbc.UPF, K.pz-n-vbc.UPF (1-valence), K.pz-sp-kjpaw_psl.0.1.UPF (9-valence), Al.pz-n-kjpaw_psl.0.1.UPF, Si.pz-n-kjpaw_psl.0.1.UPF, and O.pz-n-kjpaw_psl.0.1.UPF. For GBRV and PSL pseudopotentials, the kinetic energy was set at 60 and 75 Ry, and charge-density cutoff was set at a multiple of 10 and 4 of kinetic energy cutoff, respectively.

The minerals (and their formulas) investigated here are orthoclase (KAl\(_2\)Si\(_3\)O\(_8\)), microcline (KAl\(_2\)Si\(_3\)O\(_8\)), albite (NaAl\(_2\)Si\(_3\)O\(_8\)), anorthite (CaAl\(_2\)Si\(_3\)O\(_8\)), muscovite (KAl\(_2\)Si\(_3\)\(_2\)H\(_4\)), illite (KAl\(_2\)Si\(_3\)O\(_1\)\(_2\)), phlogopite (KAl\(_2\)Mg\(_2\)O\(_1\)\(_2\)), and sylvite (NaCl). Their crystal structures were taken from experiments and the lattice and atomic positions were relaxed until the total force and stress were smaller than 10\(^{-4} \) atomic units and 0.1 kbar, respectively. A phonon calculation was then performed for each structure using DFPT (density functional perturbation theory).\(^{67,74} \) The same calculations were performed for K and Rb by substituting the second for the first in the mineral structures. For albite–microcline (Na and K feldspars) solid solution and K-substituted anorthite, phonon frequencies were only calculated at the Γ point. For microcline–anorthite (K and Ca feldspars) solid solution, for every Ca-substituted by K, one Al was replaced with Si to balance charge. For aqueous K⁺, we considered configurations from molecular dynamics (MD) trajectory, only the atomic positions were relaxed.

To model infinite dilution we used two strategies. The first is what we call the constrained cell method (Rb in muscovite, orthoclase, phlogopite, and illite): (1) we fully relaxed the lattice and atomic positions of the host phase; (2) we made one substitution (i.e., replaced one K with Rb); (3) we held the lattice constant fixed but relaxed the atomic positions of the structure after substitution; and (4) we calculated the phonon frequencies and rpf. The second is the supercell approach (Rb in sylvite combines the supercell and constrained cell approaches): (1) we obtained a primitive cell; (2) we made one substitution (i.e., replaced one K with Rb); (3) we calculated the phonon frequencies and rpf; (4) we made a supercell that was twice as large as the primitive cell and repeated steps 2 and 3; (5) we made another supercell that was twice as large as the cell in the previous step and repeated steps 2 and 3; and (6) we repeated step 5 until 1000 ln \( \beta \) converged.

One caveat when using the constrained cell approach to study infinite dilution is that the primitive cell must be relatively large so there is minimal interaction between substituents. In cases like KCl, where there are 2 atoms in the primitive cell, one still needs to build a supercell. For Rb-sylvite, we used tetragonal K\(_x\)Cl\(_8\) with one Rb atom substituting for K.
3. RESULTS

The structures of minerals investigated here are provided in Figure 1, and the mineral lattice parameters calculated from first-principles are given in Table S1. The PDOS of the minerals are given in the Supporting Information (Figure S1). We also report the calculated frequencies as compared to those reported by Ducher et al.,\textsuperscript{76} we found that the presence of hydrogen atoms leads to slightly distorted lattice parameters.

Figure 1. Structures (rendered by VESTA)\textsuperscript{78} of minerals and aqueous K\textsuperscript{+} investigated in this paper. Albite, anorthite, microcline, and orthoclase share the feldspar structure. Red represents O, white represents H, green represents Cl, dark blue represents Si, light blue represents F. 2 The coefficients in the expansion describing the temperature dependence of 1000 ln β, the force constant of the chemical bonds, and the 1000 ln β values at 300, 600, and 1200 K are given in Table 1 for K, Rb, and aqueous K\textsuperscript{+}. The temperature dependence of rfr is shown in Figure 2, where the rfr scales linearly with 1/T\textsuperscript{2}. The (F) values for Rb are \textasciitilde20–50\% larger than those for K in the same minerals and given the mass difference (eqs 7 and 8), we expect the ratio Δ\textsuperscript{41/37K-A/Δ\textsuperscript{41/37Rb-A} to be \textasciitilde3.5 for equilibrium fractionation between two systems A and B if K and Rb are fractionated together by an equilibrium process.

We calculated the rfr for aqueous K\textsuperscript{+} by extracting 20 snapshots (see Figure S5 for rfr convergence with respect to number of snapshots) from MD trajectories and performed phonon calculations on the relaxed snapshot structures. In the PDOS calculated for aqueous K\textsuperscript{+}, we can clearly see couplings to the H–O–H bending and O–H stretching modes at higher frequency (Figure 3).

The calculated rfr of aqueous K\textsuperscript{+} shows some variability (see Figure 2) across different snapshots due to dynamical changes in the coordination environment of K\textsuperscript{+}. In our FPMD simulation, we found that the coordination number of K\textsuperscript{+} varies from 4 to 10 between snapshots, with an average coordination number of 6.7 (Figure S2). We averaged the rfr obtained from 20 snapshots uniformly spaced in time, whose average coordination number (7.2, Figure S2) is comparable to that obtained over the whole trajectory. Similar to the results of Ducher et al. for solvated Zn, we found little correlation that obtained over the whole trajectory. We also assume that the dependence of rpfr is shown in Figure 2, where the rpfr scales linearly with 1/|Δ|.

Table 1. Force Constants for K and Rb (Infinite Dilution in K-Bearing Minerals), Expansion Coefficients for 1000 ln β = A\textsubscript{x} + A\textsubscript{x}\textsuperscript{2} + A\textsubscript{x}\textsuperscript{3} With x = 10\textsuperscript{6}/T\textsuperscript{2}, and 1000 ln β Values at Selected Temperatures

<table>
<thead>
<tr>
<th></th>
<th>(F) (N/m)</th>
<th>A\textsubscript{1}</th>
<th>A\textsubscript{2}</th>
<th>A\textsubscript{3}</th>
<th>300 K ln β</th>
<th>600 K ln β</th>
<th>1200 K ln β</th>
</tr>
</thead>
<tbody>
<tr>
<td>muscovite</td>
<td>K</td>
<td>0.169</td>
<td>–3.25 x 10\textsuperscript{-4}</td>
<td>3.84 x 10\textsuperscript{-6}</td>
<td>1.875</td>
<td>0.469</td>
<td>0.117</td>
</tr>
<tr>
<td></td>
<td>Rb</td>
<td>0.043</td>
<td>–6.54 x 10\textsuperscript{-5}</td>
<td>8.11 x 10\textsuperscript{-7}</td>
<td>0.474</td>
<td>0.119</td>
<td>0.030</td>
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<td>0.152</td>
<td>–3.07 x 10\textsuperscript{-4}</td>
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<td>1.690</td>
<td>0.423</td>
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<td>8.87 x 10\textsuperscript{-7}</td>
<td>0.508</td>
<td>0.127</td>
<td>0.032</td>
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<td>sylite</td>
<td>K</td>
<td>0.148</td>
<td>–8.40 x 10\textsuperscript{-5}</td>
<td>7.47 x 10\textsuperscript{-6}</td>
<td>1.643</td>
<td>0.411</td>
<td>0.103</td>
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<tr>
<td></td>
<td>Rb</td>
<td>0.047</td>
<td>–2.26 x 10\textsuperscript{-5}</td>
<td>2.02 x 10\textsuperscript{-6}</td>
<td>0.517</td>
<td>0.129</td>
<td>0.032</td>
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<tr>
<td>phlogopite</td>
<td>K</td>
<td>0.144</td>
<td>–2.97 x 10\textsuperscript{-4}</td>
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<td>1.605</td>
<td>0.401</td>
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<td>0.042</td>
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<td>0.116</td>
<td>0.029</td>
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<tr>
<td>[K\textsubscript{2}(\text{H}_{2}\text{O})\textsubscript{4}]	extsuperscript{+}</td>
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<td>–4.61 x 10\textsuperscript{-4}</td>
<td>6.24 x 10\textsuperscript{-6}</td>
<td>1.610</td>
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<td>2.093</td>
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<td>K</td>
<td>0.263</td>
<td>–9.47 x 10\textsuperscript{-4}</td>
<td>1.34 x 10\textsuperscript{-5}</td>
<td>2.829</td>
<td>0.725</td>
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<td>microcline–albite 12.5% K</td>
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<td>–7.55 x 10\textsuperscript{-4}</td>
<td>7.06 x 10\textsuperscript{-6}</td>
<td>3.150</td>
<td>0.803</td>
<td>0.202</td>
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<tr>
<td>albite 0% K</td>
<td>K</td>
<td>0.295</td>
<td>–4.32 x 10\textsuperscript{-4}</td>
<td>1.32 x 10\textsuperscript{-6}</td>
<td>3.225</td>
<td>0.816</td>
<td>0.205</td>
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<tr>
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<td>K</td>
<td>0.329</td>
<td>–5.98 x 10\textsuperscript{-4}</td>
<td>2.48 x 10\textsuperscript{-6}</td>
<td>3.584</td>
<td>0.909</td>
<td>0.228</td>
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<tr>
<td>anorthite 0% K</td>
<td>K</td>
<td>0.388</td>
<td>–9.61 x 10\textsuperscript{-4}</td>
<td>5.34 x 10\textsuperscript{-6}</td>
<td>4.203</td>
<td>1.071</td>
<td>0.269</td>
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</table>

Albite 0\% K, anorthite 0\% K, Rb-muscovite, orthoclase, phlogopite, and illite were calculated using the constrained cell approach. Rb-sylvite was calculated using a combination of the supercell and constrained cell approaches.
4. DISCUSSION

To the best of our knowledge, there is no calculation of rpfr for Rb with which we could compare our results, nor could we find any experimentally measured, direct determination of equilibrium intermineral fractionation data for Rb. The most relevant comparisons are a theoretical study on alkali feldspar by Li, Y. et al.\textsuperscript{45} and the work of Li, W. et al. on K fractionation between salts and aqueous solution.\textsuperscript{22} We will first discuss and compare our results to both studies and then present the implications of our results.

4.1. Mineral Fractionation: Comparison with a Previous Theoretical Study. Li, Y. et al. examined the influence of the Na–K solid solution in alkali feldspar by calculating the rpfr of K in K-feldspars using DFT and the LDA functional and pseudopotentials. To make the discussion more straightforward, we converted the expansion coefficients reported by Li, Y. et al. to force constants (see eqs 4 and 5). For K in microcline, they obtained a force constant of 48 N/m, while for Na–Rb in NaCl, the value is 64 N/m. These values are significantly larger than the values of 28 and 35 N/m that we obtained for the same minerals using PBE. Li, Y. et al. claimed that the LDA approximation is more appropriate because it gave better agreement between computed and experimental lattice parameters, and the rpfr is inversely proportional to the unit cell volume.\textsuperscript{45} One potential concern in Li, Y. et al.’s study is the use of 1-valence pseudopotentials for the alkali atoms (Na and K), as it is well known that considering only the outermost valence electrons of these elements may cause significant errors in most computed properties.\textsuperscript{5,79,80} To evaluate the influence of such pseudopotentials, we tested 3 sets of LDA pseudopotentials from different libraries for microcline. The three sets of LDA pseudopotentials are (1) a set from the Quantum ESPRESSO PSLibrary (PSL1) that uses 1-valence alkali pseudopotentials as used by Li, Y. et al.; (2) a set from Quantum ESPRESSO PSLibrary (PSL9), in which we used 9-valence alkali pseudopotentials—the only difference between PSL9 and PSL1 is the alkali pseudopotential; and (3) one set from the GBRV pseudopotential library that has 9-valence alkali pseudopotentials. The resulting cell parameters, unit cell volume, and the force constant for microcline are shown in Table 2 and compared with the experimental results. Temperature-dependent 1000 ln $\beta$ values are given in Figure 4. First, we note that the result reported by Li, Y. et al. was reproduced when using the pseudopotential set PSL1 (Table 2). We found that two different sets of pseudopotentials with 9-valence alkali pseudopotentials gave similar lattice parameters and rpfr with the experimental results. Temperature-dependent 1000 ln $\beta$ values are given in Figure 4. First, we note that the result reported by Li, Y. et al. was reproduced when using the pseudopotential set PSL1 (Table 2). We found that two different sets of pseudopotentials with 9-valence alkali pseudopotentials gave similar lattice parameters and rpfr.

Table 2. Experimental and Calculated Lattice Parameters with Different Pseudopotentials, Unit Cell Volume, and Force Constant of K-Bonds (Which Controls Equilibrium Isotopic Fractionation through Eq 7; gamma-point only calculation) for Microcline

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$V_{\text{cell}}$ (%)</th>
<th>$\langle F \rangle$ (N/m)</th>
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<tbody>
<tr>
<td>exp. measured</td>
<td>8.571</td>
<td>12.964</td>
<td>7.221</td>
<td>720.99</td>
<td>0.0</td>
<td>N/A</td>
</tr>
<tr>
<td>Li et al.\textsuperscript{45}</td>
<td>8.600</td>
<td>12.942</td>
<td>7.199</td>
<td>717.79</td>
<td>-0.4</td>
<td>48</td>
</tr>
<tr>
<td>LDA-PSL1</td>
<td>8.633</td>
<td>12.928</td>
<td>7.208</td>
<td>722.17</td>
<td>0.2</td>
<td>45</td>
</tr>
<tr>
<td>LDA-PSL9</td>
<td>8.417</td>
<td>12.901</td>
<td>7.180</td>
<td>699.61</td>
<td>-3.0</td>
<td>38</td>
</tr>
<tr>
<td>LDA-GBRV</td>
<td>8.425</td>
<td>12.917</td>
<td>7.186</td>
<td>702.12</td>
<td>-2.6</td>
<td>38</td>
</tr>
<tr>
<td>PBE</td>
<td>8.698</td>
<td>13.105</td>
<td>7.313</td>
<td>752.03</td>
<td>4.3</td>
<td>28</td>
</tr>
</tbody>
</table>
Although this diﬀerence could be explained by the diﬀerence in predicted unit cell volumes, compared with the results obtained with PBE, Using LDA pseudopotentials from GBRV libraries, we conducted another test with a 50–50 microcline–albite structure as reported by Li, Y. et al., and we again obtained a smaller force constant (49 N/m) than that reported by Li, Y. et al. (64 N/m). Finally, we tested the PSL1 PP for the NaCl structure of sylvite and found that total energy convergence could not be achieved even with kinetic energy cutoff set at 120 Ry (Figure S3).

We further calculated r-pr for K in the microcline–albite, and microcline–anorthite solid solution (Figure 5) with PBE pseudopotentials. We consistently found a ~40% diﬀerence in absolute 1000 ln β values calculated with LDA and PBE, which could be explained by the diﬀerence in predicted unit cell volume as suggested by Li, Y. et al. Although this diﬀerence might appear concerning, when the intermineral fractionation (ΔΛ–β) is considered, a much smaller diﬀerence is obtained (Figure S4) if the same functional is used in the calculation of r-pr because LDA/PBE consistently underestimate/overestimate lattice parameters.77

The results presented above suggest that the diﬀerence between our ﬁndings and those of Li, Y. et al. is due to the use of LDA or PBE approximation, as well as the use of pseudopotentials for the metal ions. We suggest that the 1-valence pseudopotential used by Li, Y. et al. is ill-suited and we recommend using state-of-the-art pseudopotential libraries in calculations of r-pr.63,81,82

4.2. Mineral/Water Fractionation: Comparison with Experiments. While the database of K isotope measurements of sediments and products of weathering is rapidly expanding,19–21 the r-pr of K+ in aqueous media has not been studied. The most relevant data that we can compare our calculations with are the experimental results from Li, W. et al., who studied equilibrium isotopic fractionation of K between soluble K-salts and their saturated solutions, a proxy for aqueous K+.22

Li, W. et al. found indistinguishable K fractionation between sylvite and aqueous K+. One concern with such experiments is that achieving equilibrium between phases at room temperature can be diﬃcult. Our calculated r-pr indicates that sylvite and aqueous K+ have indistinguishable fractionation at room temperature, given the current analytical precision on δ41K measurements (~0.1‰). Our results thus agree well with the experimental results of Li, W. et al.

One potential concern is that Li, W. et al. used saturated sylvite solution while in our calculation K+ is not saturated. However, we do not expect the concentration to have a signiﬁcant impact based on the study by Wang et al.,83 which shows that an increase in the simulation concentration of Mg2+ from 1 Mg in 50 H2O to 1 Mg in 30 H2O only increases the r-pr of Mg by ~3‰.

4.3. Mineral/Water Fractionation: Implications. Wang et al. reported a K isotopic fractionation between seawater and the BSE of δ41K = +0.6‰.84 The residence time of K is on the order of 10 Myr,85 indicating that although only a handful of measurements were reported, they are likely representative of Earth’s oceans as a whole because the ocean mixing timescale is only around 1 kyr.80 The heavy isotope enrichment in seawater most likely involve K isotopic fractionation (kinetic or equilibrium) between solvated K+ and minerals, either during terrestrial weathering71,83,84 or due to
uptake in silicate minerals in sediments and hydrothermal systems.\textsuperscript{39–42} Li, S. et al. evaluated the global mass-balance of K in the oceans using $\delta^{41}$K values of the sources and sinks as inputs.\textsuperscript{25} They found that potassium dissolved in river waters seems to be shifted in its $\delta^{41}$K value by $+0.55 \pm 0.29\%e$ relative to the clay fraction in the same rivers, and globally, the $\delta^{41}$K value of rivers is $-0.22 \pm 0.04\%e$, which is shifted by $\sim +0.3\%e$ relative to the BSE, which has a $\delta^{41}$K value of $\sim -0.52$.\textsuperscript{18,25,38} The riverine $\delta^{41}$K value is low relative to the seawater value of $\sim +0.06 \pm 0.10\%e$,\textsuperscript{37} which corresponds to a seawater-riverine run off difference in $\delta^{41}$K values of $+0.28 \pm 0.11\%e$. There is insufficient data available at present to evaluate what processes affect K isotopes on a global scale, which is important if one wants to transfer knowledge of the present terrestrial cycle to the geological record.

Our calculation of the K isotopic fractionation between solvated K$^+$ and illite allows us to partially address this question. At a temperature of 25 °C relevant to weathering at the surface of continents, we calculate an equilibrium $\delta^{41}$K fractionation between water and illite of $+0.24\%e$. At a higher temperature of 100 °C relevant to hydrothermal systems or smectite-illite conversion in sediments ($\sim 50$–100 °C), we calculate a fractionation of $+0.16\%e$. The K inputs in the oceans comprise (1) continental weathering and (2) mid ocean ridge hydrothermal fluxes. The sinks that remove K from the oceans are (1) the formation of K-bearing authigenic clays and ion exchange during sediment diagenesis and (2) low temperature basalt alteration. Given the elevated temperatures involved in hydrothermal systems, it is unlikely that the hydrothermal flux has a $\delta^{41}$K value higher than seawater to balance the low $\delta^{41}$K value of the rivers. To explain the elevated $\delta^{41}$K value of seawater relative to the sources (rivers and mid ocean ridges), there must therefore be a negative fractionation between the K sinks and seawater ($\delta^{41}$K$_{sinks} - \delta^{41}$K$_{seawater} < 0$). Li, S. et al. estimated that the isotopic fractionation between sediments (formation of authigenic clays and ion exchange) and seawater must be $-0.6$ to $-0.3\%e$.\textsuperscript{53} The equilibrium fractionation that we calculate between illite and solvated K$^+$ is $-0.24\%e$, which could explain the seawater value if the $-0.3\%e$ shift between sediment and seawater was the correct number or would be insufficient if the shift was actually $-0.6\%e$ (but it could still contribute to $\sim$ half of the overall shift). Further work is clearly needed to better constrain the global geochemical cycle of K. In particular, combining K and Rb isotopic analyses could provide new insights into these processes.

4.4. Teasing Apart Equilibrium and Kinetic Processes from Combined K and Rb Fractionations. The most straightforward manner to compare K and Rb equilibrium isotopic fractionations is to compare the strength of the bonds that they form. To the best of our knowledge, the only nominal Rb-bearing natural mineral is rubidium (Rb-rich microcline). The reason for this scarcity is the low abundance of Rb, which always substitutes for K in K-bearing minerals. To model the low Rb concentration in natural samples (the K/Rb weight ratio on Earth is 400),\textsuperscript{4} we studied Rb in K-bearing mineral lattices (see Method section for details). As seen in Figure 6, the force constants of Rb in a variety of minerals are relatively constant and are $\sim 20$–50% larger than those of K. Given the strength of K and Rb chemical bonds, and the relative mass differences between $^{87/85}$Rb and $^{41/39}$K, we would thus expect the isotopic compositions of two phases A and B in equilibrium to be related through the relationship\textsuperscript{86,87}

\begin{equation}
\Delta^{41/39}K_{A-B} \approx c \cdot \Delta^{87/85}Rb_{A-B}
\end{equation}

where $c$ is $\sim 3.5$ depending on the host phase. Although K and Rb are chemically similar, they do not necessarily behave in the same way during geochemical processes. For instance, plagioclase is known to preferentially partition K relative to Rb,\textsuperscript{38} and Rb is preferentially incorporated in alteration phases (e.g., polygonite, smectite) during alteration on the seafloor.\textsuperscript{31,32,40,89} These kinetic processes have been discussed extensively in the context of fractionation between isotopes (e.g. the relationship between $\delta^{17}$O and $\delta^{18}$O)\textsuperscript{87,92,93} and the same reasoning can be applied to K and Rb.

By combining K and Rb isotopic analyses, it is potentially possible to determine whether K and Rb isotopic fractionations are controlled by kinetic or equilibrium processes. To illustrate this, we have performed a simple calculation of K and Rb isotopic fractionation due to diffusion in water, which could be representative of diffusion through porewater in sediments, which Santiago-Ramos et al.\textsuperscript{21} argued could be a cause of the elevated $\delta^{41}$K value of seawater if light K isotopes diffuse faster than heavy ones. The ratio of the diffusion coefficients $D_i$ and $D_j$ of two isotopes $i$ and $j$ depend on their masses $m_i$ and $m_j$ through\textsuperscript{54}

\begin{equation}
\frac{D_i}{D_j} = \left(\frac{m_j}{m_i}\right)^b
\end{equation}

where $b$ is a coefficient that is derived from fitting results from experiments or MD simulations ($b = 0.049$ for K diffusion in aqueous medium, from MD simulation).\textsuperscript{95} The diffusivity of K in water is $3.85 \times 10^{-9} \text{ m}^2/\text{s}$ (MD simulation, from literature).\textsuperscript{96} Due to lack of data, we further model Rb as a heavier potassium isotope given that K and Rb have similar properties.
chemical properties and K and Cs have similar diffusion coefficients,\(^5\) which leads to a diffusivity of Rb in water at 25 °C of 3.70 \times 10^{-9} \text{ m}^2/\text{s}. We compute K and Rb isotopic fractionation assuming 1D diffusion between two semi-infinite media with initial concentrations \(C_0 = 0 \) (x < 0) and \(C_x = 0.2 \) M (x > 0). In these conditions, the isotopic fractionation is given by the following equation\(^96\)

\[
\delta^{i/j} (\% \boldsymbol{e}) = -250 \left( \frac{m_j}{m_i} - 1 \right) \exp(-u^2/4) \left( \frac{bu/{\sqrt{\pi}}}{0.5 \text{ erfc}(u/2) - 1} \right)
\]

where \(u = x/\sqrt{D}t\) is dimensionless time (the solution is self-similar, meaning that the isotopic profile stretches in space with the square root of time).

As shown in Figure 7, the kinetic isotopic fractionation produced by diffusion of K and Rb yields \(\delta^{\text{41K}}/\delta^{\text{87Rb}} = 2.2, \) relatively small fractionation between silicate melts and crystallized minerals. Assuming that the force constants of K and Rb between silicate melts and crystallized minerals differ by 35 and 7 \text{n/m} respectively, based on the values calculated for silicate minerals, we estimate that at 1100 °C, the equilibrium fractionation between silicate melt and mineral should be lower than 0.10%\(\text{e}\) for \(\delta^{\text{41K}}\) and 0.006%\(\text{e}\) for \(\delta^{\text{87Rb}}\). Using a lower temperature of 900 °C, one would expect the equilibrium isotopic fractionations between silicate melt and mineral to be lower than 0.14 and 0.009%\(\text{e}\) for \(\delta^{\text{41K}}\) and \(\delta^{\text{87Rb}}\), respectively. For comparison, K and Rb isotopic compositions can be measured with precisions of ~0.1 and 0.03%\(\text{e}\), respectively.\(^17\sim23,34,37,38\) Partial melting and magmatic differentiation processes are thus unlikely to be associated with significant equilibrium isotopic fractionations for K and Rb.

If any large isotopic fractionation is found for these systems at magmatic temperatures, it is therefore likely to be the product of kinetic isotope effects associated with diffusive transport.\(^103\) For example, laboratory experiments have shown that K isotopes could be readily fractionated by Soret diffusion in silicate melts at high temperature, with a fractionation of 1.06%\(\text{e}/\text{amu}\) per 100 °C gradient.\(^103,104\) While equilibrium isotopic fractionation decreases as the inverse of the square of the temperature, diffusion in silicate can impart large isotopic fractionation even at magmatic temperatures. Such fractionation has been extensively documented in olivine for Mg and Fe.\(^105\sim109\) The geological settings where K and Rb diffusion could happen at high temperature involve (1) large-scale diffusive transport in the mantle where solids and melts interact, as documented for Li and Fe (e.g., through metasomatism),\(^110\sim113\) (2) transport of K-rich aqueous fluids from the subducting slab to the mantle wedge where those fluids can induce flux melting, and (3) late diffusive re-equilibration of xenoliths\(^114\) or zoned minerals with their host melts.\(^105\sim109\) Again, the correlation between K and Rb isotopic fractionations in magmatic systems could provide insights into whether these fractionations are driven by equilibrium or kinetic processes.

5. Conclusion

We report a thorough first-principles study of equilibrium fractionation properties of aqueous K\(^+\), K, and Rb in common K-bearing minerals using DFT and FPMD. The motivation for this work is to provide a framework for interpreting the isotopic variations documented in natural systems for K and Rb.

In water, we do not find a clear correlation between the strength of the K bonds and the coordination number. The mean force constant of K-bonds in water is ~25 \text{N/m}. This falls within the range of force constant values calculated by us and others for K-bearing minerals (between 22 and 30 \text{N/m}, not including solid solution, Table 1).

The value of rpf\(f\) computed for sylvite is in good agreement with a previous study; however, the rpf\(f\) value of feldspar differs significantly from that reported in the literature. We ascribe the difference to the choice of the pseudopotential. Our description of the valence-core partition is more accurate but the overall accuracy of the theory, in particular the functional used, remains to be fully tested. We emphasize, however, that any error present in DFT calculation of the absolute value of the rpf\(f\) is substantially reduced when calculating equilibrium isotopic fractionation factors between phases (Figure S4), as this results in a partial cancellation of systematic errors.

![Figure 7](image-url)
We also calculate the force constants of Rb in nominal K-bearing minerals. The force constants of Rb in the minerals investigated here are slightly larger than those for K, indicating that in most systems, equilibrium isotopic fractionation between two phases A and B should be characterized by a ratio $\delta^{138}\text{Rb}_A/\delta^{138}\text{Rb}_B$ of approximately 3–4. We show through a diffusion calculation relevant to K and Rb diffusion in sediment porewater that kinetic isotopic fractionation would depart from the equilibrium value; hence measuring K and Rb isotopic ratios together with K/Rb ratios could provide new insights into the drivers of K and Rb fractionations in natural systems.

Based on the computed rpfr, we obtained the equilibrium K isotopic fractionation between aqueous K$^+$ and illite, taken as a proxy mineral for clays. At 25 °C, the fractionation is +0.24‰, suggesting that equilibrium fractionation between aqueous K$^+$ and K-bearing clay minerals is insufficient to explain the observed K heavy isotope enrichment in seawater or river waters. Instead, this heavy K isotope enrichment could partly reflect kinetic isotopic fractionation associated with diffusive transport or unidirectional chemical reactions.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.9b00180.

1. PDOS for minerals investigated; (2) calculated and experimental lattice parameters for minerals; (3) coordination number of aqueous K$^+$; (4) test of total energy convergence for the NaCl structure with respect to kinetic energy cutoff; (5) 1000 ln β calculated by LDA and PBE for K in albite–microcline solid solution; (6) convergence of 1000 ln β with respect to number of snapshots used for calculation; and (7) calculated versus measured infrared and Raman frequencies of K-bearing minerals (PDF).

Partial phonon density of states of all atoms in the snapshots used for calculation; and (7) calculated versus number of atoms.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: dauphas@uchicago.edu.

**ORCID**

Tuan Anh Pham: 0000-0003-0025-7263

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### ABBREVIATIONS

rpfr, reduced partition function ratio; LDA, localized density approximation; BOMD, Born–Oppenheimer molecular dynamics; MD, molecular dynamics; DFT, density functional theory; DFPT, density-functional perturbation theory

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