

AB INITIO APPROACH TO EQUILIBRIUM FRACTIONATION OF K AND RB

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Introduction: Recent advancement in mass spectrometry and purification protocols now allow the isotopic compositions of K and Rb to be measured with sufficient precisions to detect naturally occurring isotopic variations in planetary material.¹⁻⁵ Potassium in particular has proven to be a useful tool in studies of seafloor alteration, volatile-element depletion, and lunar formation.^{2,4,6,7} Both belonging to the alkali earth group, Rb and K have very similar chemical and physical properties, and due to its relative low abundance, Rb usually substitutes for K in solids and liquids (e.g., feldspar). We therefore hypothesized Rb shared similar fractionation properties as K but because of their different masses, the combined use of K and Rb could shed some light on the processes acting on alkalis in nature. Specifically, what additional piece of information does Rb isotopic fractionation convey that is not already known from K? Recent measurements have revealed heavy isotope enrichments in both K and Rb in lunar rocks relative to mantle-derived terrestrial rocks. An important and timely question is whether those variations can reflect equilibrium processes.

We report calculations of the equilibrium fractionation factors of Rb and K in common K-bearing minerals, and aqueous K⁺ using density functional theory (DFT) and first-principle molecular dynamics (FPMD). We also examine the importance of using properly tested pseudopotentials in theoretical studies by comparing our results with a recent theoretical study from Li et al.⁸

Method: The equilibrium isotopic fractionation of an element Y between two phases a and b can be written in the form of reduced partition functions (β) ratios:

$$\alpha(a, b, Y) = \frac{\beta(a, Y)}{\beta(b, Y)}$$

β factors can be computed from the vibrational frequencies through the following:

$$\beta = \left(\prod_{i=1}^{3N} \prod_q \frac{v_i}{v'_i} \times \frac{e^{-\frac{h\nu_{q,i}}{2kT}}}{1 - e^{-\frac{h\nu_{q,i}}{kT}}} \times \frac{1 - e^{-\frac{h\nu'_{q,i}}{kT}}}{e^{-\frac{h\nu'_{q,i}}{2kT}}} \right)^{\frac{1}{nN_q}}$$

where $\nu_{q,i}$ is the vibrational frequency of the vibrational mode i at wave vector q , N is the number of atoms in the unit cell, n is the number of isotopes, and N_q is the number of q points.⁹

FPMD simulation of aqueous K⁺ was carried out by Qbox code.¹⁰ The water box was created to reproduce the density of water and contain 63 water molecules and

1 potassium ion. 20 snapshots uniformly spaced in time were extracted from the trajectory.

Unless otherwise specified, computations (structural relaxation and phonon calculation) were carried out by Quantum ESPRESSO,^{11,12} with plane-wave basis set, Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation (GGA),¹³ and norm-conserving pseudopotentials from ONCV library.¹⁴ For comparison with results from Li et al., we also used local density approximation (LDA) based pseudopotentials from GBRV library and Quantum ESPRESSO pseudopotential data base.^{15,16}

All mineral structures were taken from experiments,¹⁷⁻²¹ and their lattice parameters and atomic positions were relaxed. Then, a phonon calculation was performed for each structure. For aqueous potassium, only atomic positions were relaxed.

Results: The calculated K-bearing mineral lattice parameters are given in Table 1. Similar to the results reported by Ducher et al.,²² we found that when hydrogens are present, lattice parameters are slightly more distorted. Otherwise, they are 1-2% larger than experimental results, which is consistent with the general trend of GGA-PBE functionals. The temperature dependence of the reduced partition functions for K is shown in Figure 1. As expected, at high temperature, $1000 \ln \beta$ scales as $1/T^2$, with the force constant (in N/m) of the bonds as the proportionality constant.

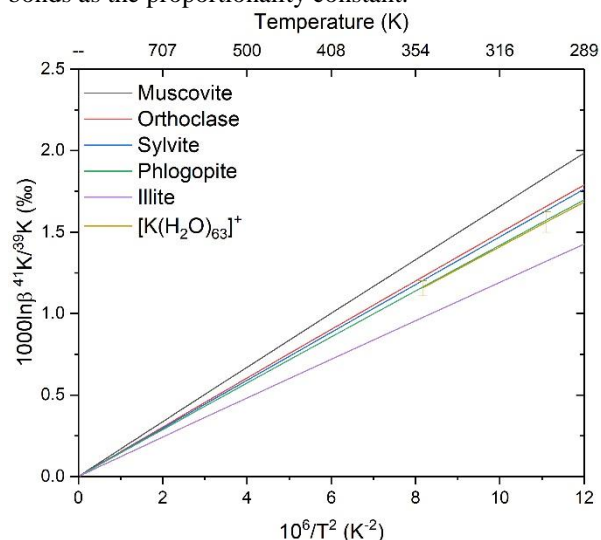


Figure 1. Calculated reduced partition functions for common K-bearing minerals and aqueous K⁺.

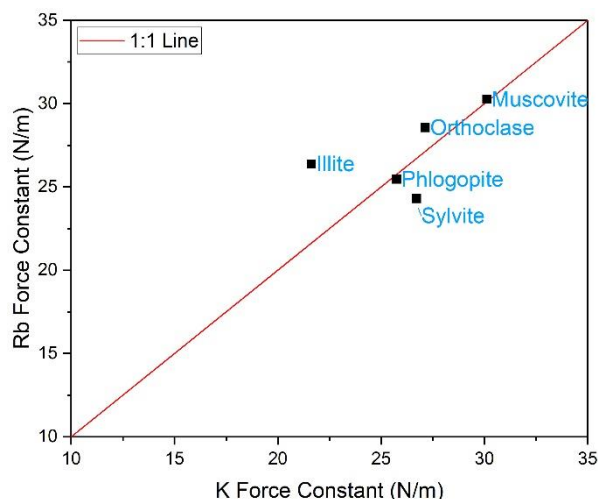


Figure 2. Calculated force constants for Rb and K in different minerals.

Discussion:

Comparison with a previous theoretical study. Li et al. argued that LDA was more appropriate than GGA for alkali feldspar since LDA better agrees with experimentally measured lattice parameters.⁸ However, their results are based on 1-valence alkali pseudopotentials, leading to an overestimation of beta factors and lattice parameters. With proper choice of pseudopotentials, LDA and GGA give lattice parameters with similar relative errors, and it is difficult to judge the quality of LDA and GGA from this perspective. Although LDA seems to describe infrared spectra at low wavenumbers more accurately, LDA produces intolerable errors when describing water systems.²³ Using GGA would make it possible to consider fractionation between minerals and aqueous species.

Equilibrium fractionation properties for K and Rb. As shown in Figure 2, except for illite, the strengths (force constants) of the harmonic bonds holding K and Rb in position are very similar. It is not yet clear to us what caused the relatively large difference in illite. Since these two elements have very different masses, their equilibrium fractionations differ and are related by a proportionality constant of 4.5, meaning that the value of $1000\ln\beta$ for K is approximately 4.5 times larger than that of Rb, which is what we would expect if Rb is merely heavier K (namely, if the only difference between Rb and K is their atomic mass). Therefore, for any equilibrium fractionation process involving both K and Rb, we should expect difference of about a factor of 4.

Summary: K and Rb are geochemical twins. We show here that these two elements form bonds of very similar strengths, meaning that at equilibrium, the $1000\ln\beta$ value of K will be a factor of 4.5 larger than that of Rb. Some implications of those results for our

understanding of the geochemical and cosmochemical behaviors of K and Rb will be discussed at the time of the conference.

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