

FIRST-PRINCIPLE COMPUTATIONS OF EQUILIBRIUM POTASSIUM ISOTOPIC FRACTIONATION IN ORTHOCLASE. H. Zeng¹, N. Dauphas¹, M. Meheut², M. Blanchard², G. Galli^{3,4}, ¹Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago (dauphas@uchicago.edu), ²Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, CNRS UMR 5563, Université Paul-Sabatier, ³Institute for Molecular Engineering, The University of Chicago, ⁴Materials Science Division, Argonne National Laboratory, IL

Introduction: The isotopic compositions of minerals and rocks provide important clues on the processes that shaped the composition of planetary bodies. As an example, Wang and Jacobsen used the heavy potassium isotopic composition of lunar rocks as evidence arguing that a high-energy and high-angular momentum giant impact scenario was responsible for the formation of the Moon, and casting some doubts on the canonical model.^[1] Experimentally examining some of the processes responsible for fractionating isotopes in lunar rocks is highly challenging due to the extreme conditions associated with the Moon forming impact.

Among various approaches to all these seemingly intractable problems, first-principle calculation based on density functional theory (DFT) has been proven to be an extremely versatile tool, which was used to investigate intricate chemical reaction mechanisms^[2] and crystal structures of material in the core of planets.^[3] Herein, we present a first-principle computation of the reduced partition function ratio (β factors) for K in potassium bearing mineral, orthoclase. The rationale for calculating the β factor for potassium in orthoclase is that during condensation of K from circumterrestrial debris to the moon, K would condense into silicates, and orthoclase is taken as the model of silicates during the formation process. We are interested in understanding how K isotopes would partition during the condensation to understand what caused K isotope variations in lunar samples and pose further constraints on the giant impact theory.

Method: The computation is based on DFT and conducted using the Quantum ESPRESSO software.^[4] Plane-wave basis set and Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)^[5] as exchange correlational functional were employed. Pseudopotentials were obtained from the ONCV library.^[6] The large size of the orthoclase unit cell, which contains 52 atoms, made the computation process time consuming and at the time of writing this abstract, the influence of some parameters are still being tested. The cutoff energy (85 Ry) and the size of a uniform Monkhorst-Pack k-point grid^[7] (3x2x3) were determined as the total energy converged within 15 meV/atom. The convergence with respect to q-point (under test and will be published in the poster) was determined as doubling the number of q points with $\ln\beta$ changing less than 0.1‰.

Starting from the experimental structure of orthoclase,^[8] the crystal structure was first relaxed until the difference in total energy between two consecutive self-consistent iterations was less than 10^{-4} Ry with a force convergence threshold 5×10^{-4} a.u. and a pressure convergence threshold 0.1 Kbar. After structural relaxation, phonon dispersion relationships for two different isotopes (³⁹K, ⁴¹K) were computed based on density functional perturbation theory (DFPT or linear response).

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

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

where $\beta(a, Y)$ is the reduced partition function ratio between phase a and a perfect gas of elemental Y. The β factors can be computed from the vibrational frequencies of a given material through following equation:^[9]

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

where $v_{q,i}$ and $v'_{q,i}$ are the vibrational frequencies of the vibrational mode i with wave vector q , N is the number of atoms in the unit cell, and N_q is the number of q points in the Brillouin zone. The calculation was done independently in Chicago and Toulouse (the parameters listed above are for the Chicago computation), so as to compare the reproducibility of the DFT calculation and the influence of some of the choices made in DFT calculations. Huang et al.^[10] previously calculated the β factor of K in orthoclase and their results differ from preliminary calculations.

Results: The relaxed lattice parameters are provided in Table 1. They agree well with experimentally measured values.^[8] A preliminary result of computed β factors from Toulouse is shown in Fig. 1 with the calculated β factor expressed in term of $\ln\beta$ and fitted against $\frac{1}{T^2}$. The Chicago results and a comparison between the two results will be presented in the conference with greater details.

	Calculation	Experiment	Difference
a (Å)	8.774	8.588	2.2%
b (Å)	13.107	13.005	0.8%
c (Å)	7.306	7.192	1.6%
beta	115.582°	116.026°	-0.4%

Table 1. Calculated and experimental lattice parameters of orthoclase (monoclinic).

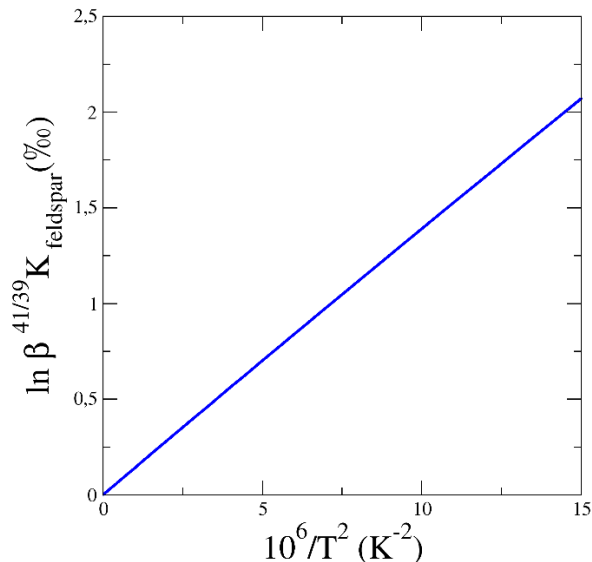


Figure 1. Calculated $\ln\beta$ versus $\frac{1}{T^2}$. The fitted relationship is $1000\ln\beta^{41/39}K = 0.143 \times \frac{10^6}{T^2}$ (Toulouse calculation; the Chicago results will be presented at the conference).

Conclusion: We provide a detailed scheme of first-principle computation of the equilibrium fractionation ratios for orthoclase. The implications of those calculations on interpretations of the K isotopic record of lunar rocks will be discussed at the conference.

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