

## First-principles investigation of the equilibrium fractionation of K isotopes among K-bearing minerals

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Researchers hold the idea that there is no K isotope fractionation [1] among terrestrial and extraterrestrial samples, until Wang and Jacobsen [2] found the  $\delta^{41}\text{K}$  of lunar rock related to Bulk Silicate Earth (BSE) is near 0.4‰. Furthermore, the larger  $\delta^{41}\text{K}$  in the HED meteorites (0.94‰) [3] and large  $\delta^{41}\text{K}$  variation in the pegmatites (>1.0‰) [4], sediments in the sea floor (~0.6‰) [5] and altered oceanic crust (~2.0‰) [6] were reported. The concentration effects [7] may be a potential reason for the large  $\delta^{41}\text{K}$  among minerals, which the  $10^3\ln\alpha$  of  $^{41}\text{K}/^{39}\text{K}$  between alkali feldspar with  $\text{K}/(\text{K}+\text{Na})=1/16$  and microcline are 2.21‰ at 300 K. However, the partial condensation, kinetic and diffusion fractionation might be others mechanisms. Therefore, the further application of K isotope fractionation need the  $10^3\ln\beta$  of K-bearing minerals especially the aqueous  $\text{K}^+$ . Used the first-principles methods, we found the  $10^3\ln\beta$  of 17 K-bearing minerals vary from 6.80‰ in alunite to 2.08‰ in djerfisherite at 300 K (decreasing in the order of alunite, K-hollandite I, niter,  $\text{K}_2\text{CO}_3$ ,  $\text{KHCO}_3$ , muscovite,  $\text{KOH}\cdot\text{H}_2\text{O}$ ,  $\text{K}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}$ , nepheline,  $\text{KOH}\cdot 2\text{H}_2\text{O}$ , kalsilite, microcline, phlogopite, lepidolite, sylvite, leucite and djerfisherite). The optimized structure of  $\text{KOH}\cdot 2\text{H}_2\text{O}$  show the O coordination number of 8 with the average K-O bond length of 2.92 Å, which is similar with aqueous  $\text{K}^+$  [8]. Regarding  $\text{KOH}\cdot 2\text{H}_2\text{O}$  as the aqueous  $\text{K}^+$ , many silicate minerals show smaller  $10^3\ln\beta$  than aqueous  $\text{K}^+$  except muscovite and nephline, which means the aqueous will carry  $^{41}\text{K}$  from silicate minerals during the hydrothermal alteration and weathering processes. This may be the reason of the large  $\delta^{41}\text{K}$  in sea and river water [9] compared with the sediments [5] and altered oceanic crust [6].

[1] Humayun & Clayton. (1995) *GCA*. **59**, 2131-2146. [2] Wang & Jacobsen (2016) *Nature*. **538**, 487-490. [3] Chen *et al.* (2018) *49<sup>th</sup> LPSC* The Woodlands, Texas. p. 1193. [4] Morgan *et al.* (2018) *J. Anal. Atom. Spectrom.* **33**, 175-186. [5] Ramos *et al.* (2018) *GCA*. **236**, 99-120. [6] Parendo *et al.* (2018) *PNAS*. **114**, 1827-1831. [7] Li *et al.* (2019) *GCA*. **245**, 374-384. [8] Azam *et al.* (2009) *J. Phys. Chem. A*. **113**, 1827-1834. [9] Lee *et al.* (2018) *Goldschmidt Abstracts*.