

Supplementary Materials for

Transmutation effects on long-term Cs retention in phyllosilicate minerals from first principles

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● Experimental thermodynamic data:

In order to calculate the energetics involved in ion-exchange reactions between K^+ , Cs^+ and Ba^{2+} species, we have used the experimental thermodynamic data listed in Table S1.

Substance	ΔH_f^0 (kJ/mol)	S_f^0 (J/mol/K)
$H^0_{(g)}$	218.00	114.72
$K^0_{(g)}$	89.24	160.34
$Cs^0_{(g)}$	76.06	175.60
$Ba^0_{(g)}$	180.00	170.24
$H^+_{(g)}$	1536.5	108.95
$K^+_{(g)}$	514.26	154.58
$Cs^+_{(g)}$	457.96	169.84
$Ba^+_{(g)}$	688.94	176.01
$H^+_{(aq)}$	0	0
$K^+_{(aq)}$	-252.38	102.50
$Cs^+_{(aq)}$	-258.28	133.05
$Ba^{2+}_{(aq)}$	-537.64	9.60

Table S1: List of the experimental thermodynamic data used. ΔH_f^0 and S_f^0 respectively represent the formation enthalpy and entropy under standard (T, P) conditions. The values in red are from the NIST-JANAF Tables,¹ while the values in black are from the Wagman *et al.* Tables.²

● Total energies of the calculated systems:

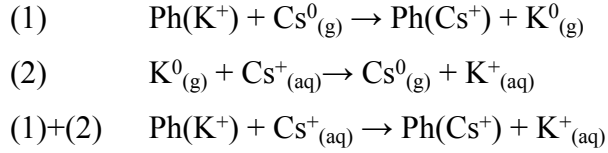
In Table S2 we report the density functional theory (DFT) calculated total energies for each charge neutral system investigated for a 2x2x1 phlogopite supercell made of 16 cation sites.

<i>Site in Row A</i>	
System [composition]	Total energy (kJ/mol)
Ph(K) – [16K,48Mg,16Al,48Si,192O,32H]	-230032.4
Phlogopite (Cs) – [1Cs,15K,48Mg,16Al,48Si,192O,32H]	-230017.7
Phlogopite (Ba) – [1Ba,15K,48Mg,16Al,48Si,192O,32H]	-230075.8
Phlogopite (Ba+V _K) – [1Ba,14K,48Mg,16Al,48Si,192O,32H]	-229938.9
Phlogopite (Ba+V _H) – [1Ba,15K,48Mg,16Al,48Si,192O,31H]	-229800.4
Phlogopite (Ba+Al _{Si}) – [1Ba,15K,48Mg,17Al,47Si,192O,31H]	-230157.0
Phlogopite (Ba+Cs) – [1Ba,1Cs,14K,48Mg,16Al,48Si,192O,32H]	-230057.5
<i>Site in Row B</i>	
System [composition]	Total energy (kJ/mol)
Ph(K) – [16K,48Mg,16Al,48Si,192O,32H]	-230032.4
Phlogopite (Cs) – [1Cs,15K,48Mg,16Al,48Si,192O,32H]	-230017.9
Phlogopite (Ba) – [1Ba,15K,48Mg,16Al,48Si,192O,32H]	-230059.9
Phlogopite (Ba+V _K) – [1Ba,14K,48Mg,16Al,48Si,192O,32H]	-229924.5
Phlogopite (Ba+V _H) – [1Ba,15K,48Mg,16Al,48Si,192O,31H]	-229788.7
Phlogopite (Ba+Al _{Si}) – [1Ba,15K,48Mg,17Al,47Si,192O,31H]	-230144.9
Phlogopite (Ba+Cs) – [1Ba,1Cs,14K,48Mg,16Al,48Si,192O,32H]	-230048.0
<i>Isolated gas phase specie</i>	
System [in a cubic box of 50 Å]	Total energy (kJ/mol)
H ⁰ _(g)	-107.4
K ⁰ _(g)	-15.2
Cs ⁰ _(g)	-12.8
Ba ⁰ _(g)	-3.0

Table S2: List of the DFT calculated total energies for each charge neutral system investigated.

- **Example of energy calculation for ion-exchange reactions:**

The case below shows how the energetics of an ion-exchange reaction has been calculated, taking the K⁺/Cs⁺ exchange in a site of row A as example. The methodology described in Rosso *et al.*,³ involves treating two step reactions in a thermodynamic cycle such that:



where equation (1) is entirely approximated using DFT calculations, as listed in Table S2. The reaction (2) represents the ionization and hydration of the cations and uses the experimental enthalpies and entropies data listed in Table S1.

- The reaction energy (ΔE_1) associated to reaction (1) is obtained by:

$$\Delta E_1 = E^{\text{DFT}}[\text{Ph}(\text{Cs}_a^+)] + E^{\text{DFT}}[\text{K}^0_{(\text{g})}] - E^{\text{DFT}}[\text{Ph}(\text{K}_a^+)] - E^{\text{DFT}}[\text{Cs}^0_{(\text{g})}] = 12.2 \text{ kJ/mol}$$

- The reaction energy (ΔE_2) of reaction (2) has been estimated by calculating the reaction enthalpy (ΔH) and entropy changes (ΔS) for the solvated cation components, such that:

$$\Delta H = \Delta H_f^0[\text{K}^+_{(\text{aq})}] + \Delta H_f^0[\text{Cs}^0_{(\text{g})}] - \Delta H_f^0[\text{Cs}^+_{(\text{aq})}] - \Delta H_f^0[\text{K}^0_{(\text{g})}] = -7.3 \text{ kJ/mol}$$

$$T\Delta S = (298.15/1000) \times (S_f^0[\text{K}^+_{(\text{aq})}] + S_f^0[\text{Cs}^0_{(\text{g})}] - S_f^0[\text{Cs}^+_{(\text{aq})}] - S_f^0[\text{K}^0_{(\text{g})}]) = -4.6 \text{ kJ/mol}$$

$$\Delta E_2 = \Delta H - T\Delta S = -7.3 + 4.6 = -2.7 \text{ kJ/mol}$$

- The overall energetics for the K^+/Cs^+ ion-exchange reaction at a temperature of 298.15 K is obtained by summing the two precedent calculations:

	Reactions	ΔE (kJ/mol)
(1)	$\text{Ph}(\text{K}_a^+) + \text{Cs}^0_{(\text{g})} \rightarrow \text{Ph}(\text{Cs}_a^+) + \text{K}^0_{(\text{g})}$	12.2
(2)	$\text{K}^0_{(\text{g})} + \text{Cs}^+_{(\text{aq})} \rightarrow \text{Cs}^0_{(\text{g})} + \text{K}^+_{(\text{aq})}$	-2.7
(1)+(2)	$\text{Ph}(\text{K}_a^+) + \text{Cs}^+_{(\text{aq})} \rightarrow \text{Ph}(\text{Cs}_a^+) + \text{K}^+_{(\text{aq})}$	9.5

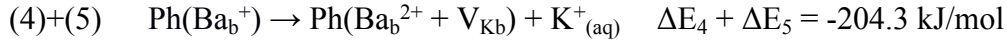
Table S3: Calculated reaction energy for the K^+/Cs^+ ion-exchange process at a temperature of 298.15 K.

- Example of energy calculation for defect formation reactions following transmutation:**

Similarly, we have used two step reactions to describe the formation of vacancy following Cs transmutation. This allows to take into account the energetics changes, such as ionization and solvation, associated to ejection of cation in aqueous environment. The example below shows how the energetics

for the creation of a K vacancy following transmutation of Cs in a site of row B have been calculated.

The two steps process can be written as:



Where the energy of reaction (4) is obtained entirely from DFT calculations (Table S2) and reaction (5) is estimated from experimental thermodynamic data (Table S1). In Figure 3b of the manuscript, the overall reaction energy (-204.3 kJ/mol) has been subtracted from the cost of Cs transmutation in a site of row B (426.4 kJ/mol), giving the final value of 222.1 kJ/mol for creating a K vacancy following transmutation.

● Chemical potentials of reference:

The reference chemical potentials, μ , for Cs^+ , Ba^{2+} , Al^{3+} , Si^{4+} , and O^{2-} were obtained from DFT calculations of Cs_2O , BaO , Al_2O_3 , SiO_2 bulk oxide materials, and the O_2 molecule, respectively. The determination of each chemical potential used the total DFT energy, noted E , as follow:

$$\mu_{\text{O}} = \frac{1}{2}E_{\text{O}_2} = -414.4 \text{ kJ/mol},$$

$$\mu_{\text{K}} = \frac{1}{2}(E_{\text{K}_2\text{O}} - \mu_{\text{O}}) = -275.6 \text{ kJ/mol},$$

$$\mu_{\text{Cs}} = \frac{1}{2}(E_{\text{Cs}_2\text{O}} - \mu_{\text{O}}) = -256.7 \text{ kJ/mol},$$

$$\mu_{\text{Ba}} = E_{\text{BaO}} - \mu_{\text{O}} = -725.1 \text{ kJ/mol},$$

$$\mu_{\text{Al}} = \frac{1}{2}(E_{\text{Al}_2\text{O}_3} - 3\mu_{\text{O}}) = -1183.0 \text{ kJ/mol},$$

$$\mu_{\text{Si}} = \frac{1}{2}(E_{\text{SiO}_2} - 2\mu_{\text{O}}) = -1459.2 \text{ kJ/mol}$$

● References:

- (1) M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**, 1.
- (2) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data*, 1982, **11**, 1.
- (3) K. M. Rosso, J. R. Rustad and E. J. Bylaska, *Clays Clay Miner.*, 2001, **49**, 500.