Alkali Cation Selectivity and Fixation by Clay Minerals

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Abstract: Two variables must be considered when calculating exchange free energies ($\Delta G^0 ex$) for 2:1 clays: (1) anionic field strength, as expressed by equivalent anionic radius (r_a), and (2) interlayer water content, as expressed by interlayer molality. For smectites that are in a state of high hydration, interlayer molality is determined by the cations undergoing exchange. Thus $\Delta G^0 ex$ for an exchanging cation pair can be calculated solely from measurements of r_a. r_a is related to layer charge per half unit cell (C) and *ab* unit cell area(A) by: $r_a = (-A/8\pi C)^{1/2}$. The layer charge necessary for cation fixation can be predicted by calculating the r_a at which cation exchange with an illite structure expresses a $\Delta G^0 ex$ equal to that of exchange with a smectite structure. The theory can also be applied qualitatively to understand the high selectivity of illite for Cs^+, the fixation of K^+ rather than Na^+ in shales during diagenesis, the stability of illite over muscovite in the weathering environment, and cation segregation in smectite.

Key Words: Cation exchange • Cation fixation • Cation selectivity • Equivalent anionic radius • Free energy of exchange • Illite • Smectite