Effect of temperature on oxyanion adsorption by goethite (α-FeOOH)

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Not much is known yet about the effect of temperature on oxyanion adsorption. Our previous data [1-3] suggest exothermic behavior in terms of equilibrium thermodynamics, with a shift in the oxyanion adsorption edge by about 0.2 pH units per 10° C towards the more acidic region, and thus in a weakening of the overall adsorption affinity with increasing temperature at circumneutral groundwater conditions. These results were compiled as black dots on a hypothetical linear free energy relationship (LFER, Figure 1) between the $\Delta G_{r,ads}$ of bidentate adsorption reaction of an element A oxyanion,

$2{\equiv}FeOH + H_nAO_m^{x-} + (2\text{-}n)H^+ = ({\equiv}FeO)_2AO_{m-2} + 2H_2O$

and the $\Delta G_{r,H+}$ (kJ/mol) of the aqueous deprotonation reaction for the respective oxyanion, $H_nAO_m^{x-} = H_{n-1}AO_m^{(x+1)-} + H^+$. More experiments to derive at missing critical points (e.g., for chromate) are underway to validate this relationship at higher accuracy. From this Gibbs energy of reaction based LFER relationship, one may infer the effect of temperature on adsorption of other oxyanions where no such data yet exist.

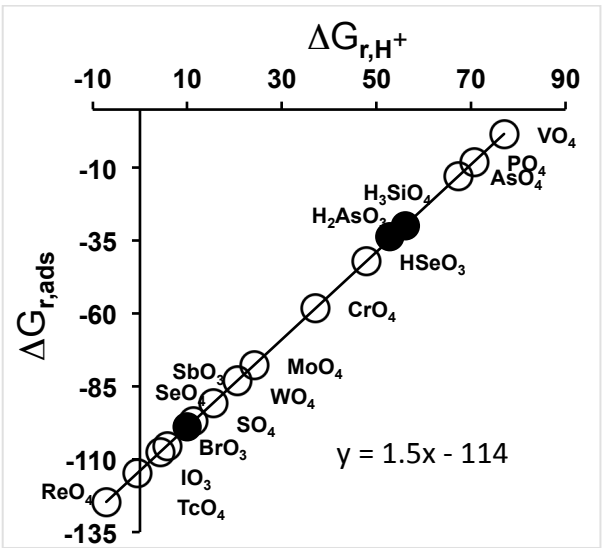

Figure 1: LFER relationship based on three black dots for experimental $\Delta G_{r,ads}$ (kJ/mol) data gained so far, while values of all open dots are predicted on basis of this correlation.

[1] Kersten & Vlasova (2009) *Appl. Geochem.* **24**, 32-43. [2] Kersten & Vlasova (2009) *Chem. Geol.* **262**, 372-379. [3] Kersten & Vlasova (2013) *Radiochim. Acta* **101**, 413-419.