

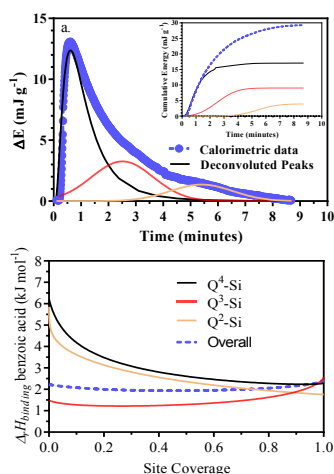
## Dynamics and Energetics of Organic–mineral interactions at the Metal Oxide-Water Interface

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The types of bonding involved in organic-mineral interactions are well understood but the in-situ evolution of their multimodal behavior and the complex outcomes produced in natural systems is not well elucidated. A flow adsorption microcalorimetry-UV (FAMC-UV) technique for studying in-situ binding of organic solutes at the mineral-water interface is presented. Results are reported for a benzoic acid (BA)-SiO<sub>2</sub> model system. Focus is on the site-specific evolution of binding kinetics, binding enthalpy and free energy of binding activation and what they tell us.

Results reflected BA binding being reversible (with water), and occurring on Si<sub>2</sub>O<sub>4</sub> (Q<sup>4</sup>), Si<sub>4</sub>O<sub>3</sub>OH (Q<sup>3</sup>) and Si<sub>4</sub>O<sub>2</sub>(OH)<sub>2</sub> (Q<sup>2</sup>) surface sites [1]. Binding on the sites followed the order Q<sup>4</sup> (54%) > Q<sup>3</sup> (32%) > Q<sup>2</sup> (14%) with pseudo-first order rate constants of 3.05, 1.58 and 1.44 min<sup>-1</sup>, respectively (Figure 1a). Overall enthalpy



of binding ( $\Delta H$ ) was  $-2.4 \text{ kJ mol}^{-1}$  (a) and associated energetics (b) for and remained benzoic acid on silica at pH 3

constant throughout. In contrast, site-specific  $\Delta H$  varied with reaction progress, eventually converging at  $-2.1 \pm 0.5 \text{ kJ mol}^{-1}$  (Figure 1b). Free energy of binding activation ( $\Delta G^{**}$ ) on the sites was  $80 \text{ kJ mol}^{-1}$ . The reversibility of BA binding, the overall low  $\Delta H$  and the positive  $\Delta G^{**}$  are all consistent with physisorption and BA favoring the solution phase than the SiO<sub>2</sub> surface. BA on SiO<sub>2</sub> is most likely on Q<sup>4</sup> and Q<sup>2</sup> sites with higher binding strength at low site coverages.

[1] Rimola, Costa, Sodupe, Lambert & Ugliengo (2013), *Chemical Reviews* 113, 4216-4313.