A mechanistic explanation for preferential binding of iron oxides to natural organic matter: Deriving free energies of binding.

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Iron oxides are widely observed associated with natural organic matter (NOM) where they e.g. are bound to humic substances and bacterial polysaccharides (BP). Iron oxides have been observed nucleating directly on NOM or they are adsorbed by it. Less stable iron oxides often transform while associated with e.g. BP because of extracellular electron transport or chemical gradients associated with the bacterial activity. The kinetics of iron oxide (trans-) formation and the resulting phases and stabilities are reported to differ from those in a pure system. To quantify the interaction strength and the thermodynamic landscape of iron oxides and NOM we used dynamic force spectroscopy to derive the free energy of binding between a model NOM molecule (alginate) and one transient and one stable iron oxide (ferrihydrite and hematite). We covalently fixed polysaccharide on an AFM tip and used the worm-like chain model to estimate the amount of molecules interacting with the iron oxide substrates. We find that a) the free energy of binding (ΔG_{bu}) is higher for the transient ferrihydrite than for the stable hematite, revealing a more favorable and stronger interaction between the model NOM and ferrihydrite (Fig); b) the interfacial free energy between the iron oxides and the model NOM is smaller in the case of ferrihydrite and c) for small contact areas (1 $Å^2$) between the model NOM and ferrihydrite, the interfacial free energy is small enough to favour nucleation. These findings provide a mechanistic explanation for the control NOM exerts on iron oxide stability and reactivity.