

Competitive adsorption and desorption of DNA on goethite in the presence of phosphate and organic matter

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The ability to extract and sequence DNA from soils and sediments provides a powerful tool to gain genetic insights into the past and present, from unravelling ancient human history to modern conservation efforts. Adsorption to mineral surfaces can protect DNA from degradation and may facilitate the long-term preservation of DNA in sediments. However, in natural systems, mineral surfaces are seldom pristine and a range of (in)organic species may co-exist in solution and compete for adsorption, affecting DNA adsorption rate, extent and mechanisms. Despite their significance, the geochemical basis and mechanistic understanding of how these competing species affect DNA - mineral interactions remain elusive, highlighting a critical knowledge gap.

We used model (in)organic competing ions, including phosphate, humic acid (HA), and the protein bovine serum albumin (BSA) to systematically investigate their impact on adsorption and desorption of DNA on goethite surfaces. Our results suggest that DNA adsorption kinetics and equilibria are influenced by DNA polymer length, concentration and nature of competing ions, and the order of addition. For example, when adsorbed first, all competing ions resulted in lower DNA adsorption, albeit to different extents (phosphate > HA > BSA), but when DNA was adsorbed first, its desorption by competition with these ions varied significantly. While phosphate, even at low concentrations, completely desorbed DNA from goethite surface, BSA and HA did not result in any significant DNA desorption even at higher concentrations. Interestingly, for smaller DNA polymers, the order of addition did not significantly impact DNA adsorption at higher phosphate concentrations, suggesting that equilibrium was reached. In contrast, the effect of HA and BSA on adsorption of DNA of all polymers sizes strongly depended on the sequence of addition, suggesting a kinetically controlled sorption over the timescales of the experiments.

This study offers mechanistic insights into the impact of competing species on DNA mobility and persistence in natural environments, highlighting that phosphate enhances DNA

mobility, potentially reducing its environmental persistence. In contrast, humics and proteins primarily reduce DNA adsorption and therefore, its adsorptive protection on minerals, when already present on mineral surfaces but are less effective at desorbing previously bound DNA.