Microbial reduction of solid-phase humic substances and electron shuttling to Fe(III) oxide

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A selection of Fe (III)-oxide stripped soils and sediments (freshwater wetland, saltmarsh, agricultural soil, and coastal plain peat) were screened for the presence of microbially (*G. sulfurreducens*) reducible solid-phase humics using an electron shuttling assay originally designed to detect dissolved reduced humics. All materials contained detectable quantities (5-50 μmol per g) of microbially reducible solid-phase humics. The solid-phase humics could also be reduced abiotically by H_2 in the presence of a palladium catalyst. Electron spin resonance showed that reduced sediments had higher signals in the range of organic radicals than non-reduced sediments. The abundance of radicals increased with increasing pH, which suggested the presence of semiquinone radicals. Addition of small amounts of humics-containing freshwater wetland sediment increased amorphous Fe (III) oxide reduction rate constants by a factor of two. Experiments conducted with cultures amended with freeze-dried surface sediment vs. cultures prepared with surface sediment porewater suggested that solid-phase humic substances were primarily responsible for the acceleration of microbial HFO reduction. Combustion of the freeze-dried sediment eliminated the stimulatory effect on Fe (III) oxide reduction. Additional experiments showed that inorganic sediment components (e.g. sand, clay, Fe (II)) were not responsible for the observed stimulation of Fe (III) oxide reduction. Experiments with pure cultures of *Geobacter* and *Shewanella* provided direct evidence for the ability of solid-phase humic substances to accelerate reduction of amorphous Fe (III) oxide. Our results suggest that microbial reduction of solid-phase humic substances may have a substantial impact on the kinetics of Fe (III) oxide reduction in organic-rich anoxic soils and sediments.

Simulating crystal nucleation: Seeing the infrequent with Molecular dynamics

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Simulating the spontaneous onset of crystalline order with molecular resolution has been a longstanding challenge, particularly for molecular systems where the nucleation and subsequent growth may be controlled by the presence of complex macromolecules. This is seen most clearly in biomineralisation, where the use of biomolecules in nature to direct the path of crystal growth leads to a degree of polymorph and morphology control that far surpasses anything that can currently be effected in a laboratory. An ability to model the onset of crystal formation at a molecular level would considerably enhance our ability to understand, and potentially to mimic, how such exquisite control of crystal form is brought about; unfortunately, the timescales on which crystal nucleation occurs is much longer than the timescales accessible to standard molecular simulation methods. This talk will show how the metadynamics method can be adapted to simulate the onset of crystal formation with statistical reliability, to extract rigorous thermodynamic information about the nucleation process and to characterise how chemical additives can modify the nucleation and subsequent growth. Several examples of applications of the method will be given, including spontaneous formation of ice in constant pressure simulations, methane hydrate formation, calcite crystallisation on self-assembled monolayers and the role of ovocleidin-17 (a protein found in the chicken eggshell) in the eggshell formation.