

Physical Organic Chemistry Relevant To Metal Ion Biogeochemistry

ALAN T. STONE¹

Department of Geography and environmental engineering
Johns hopkins university, baltimore, md 21218

Organisms exude a wide range of molecules that solubilize and alter the oxidation state and speciation of metallic elements in soils and sediments. Attention is often focused on one chemical reaction or attribute, such as the ability to adsorb to surfaces, to chelate metal ions in solution, or serve as oxidant or reductant. Other reactions or attributes might nevertheless be important. All must be considered in any assessment of a molecule's overall biogeochemical impact. The plant root exudate malonate, for example, exists predominantly as the keto tautomer, important in metal ion chelation, but the less abundant enol tautomer is responsible for its reductant reactivity. Phytosiderophores such as mugineic acid and avenic acid and the bacterial siderophore rhizobactin likely undergo a ring closure reaction termed lactamization, which impedes metal ion binding. Rates and equilibrium extents of lactamization as a function of ambient chemical conditions, e.g. pH and major ion composition, are poorly understood. During oxidations, many organic substrates yield reaction intermediates that are subject to hydrolysis, hydration, and decarboxylation. Two-equivalent reduction of manganese dioxide by the allelochemical gentisate, for example, yields carboxy-p-benzoquinone, which rapidly hydrates and tautomerizes, generating 2,3,5-trihydroxybenzoate. 2,3,5-Trihydroxybenzoate is itself subject to two-equivalent oxidation. Hydration thus converts a two-equivalent reductant into a four-equivalent reductant. Physical Organic Chemistry provides a basis for linking the identity, number, and arrangement of functional groups within a molecular structure with its reactivity. This line of inquiry is particularly important in investigations of reactions and catalysis at mineral/water interfaces, the most distinctive feature of soil and sediment microenvironments.