

Sources, sinks, and reactivity of electrophilic groups within natural organic matter

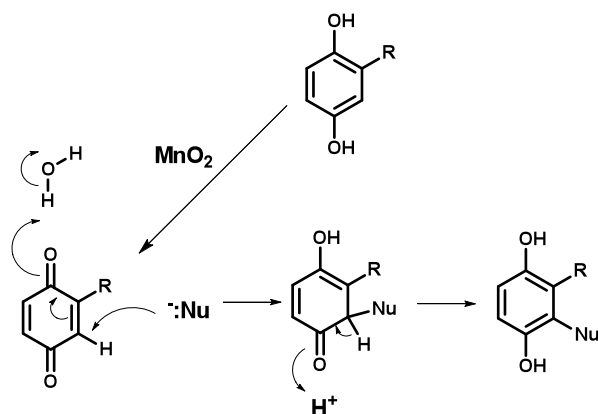
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Carbonyl and carboxylate ring substituents are believed to be present in high abundance within natural organic matter (NOM). Their potential impact on the reactivity of dihydroxybenzene/benzoquinone functionalities has not, however, been addressed. Owing to their electron-withdrawing nature, carbonyl and carboxylate ring substituents raise the redox potential necessary for oxidizing dihydroxybenzenes to corresponding benzoquinones. Carbonyl- and carboxylate-substituted benzoquinones generated in this way are far more electrophilic than unsubstituted analogs, and hence capable of Michael-type adduct formation with a wider range of oxygen-, nitrogen-, and sulfur-donor nucleophiles. Heightened electrophilicity also raises rates of competitive hydration reactions.

We have observed these phenomena in experiments employing low MW NOM surrogates. MnO_2 (pyrolusite) readily oxidizes acetoxyhydroquinone to acetoxy-p-benzoquinone and gentisate to carboxy-p-benzoquinone. Unlike unsubstituted p-benzoquinone, p-benzoquinones possessing electron-withdrawing groups rapidly hydrate. Adduct yields increase substantially as the nucleophile concentration is increased, a reflection of more successful competition relative to the hydration pathway.

Benzoquinones are one sub-class of conjugated enone carbonyls capable of Michael-type adduct formation. It is possible that oxidation reactions, e.g. by manganese(III, IV) oxyhydroxide crusts within oxic sediments, generate other reactive, transient electrophiles. Knowledge of their sources and sinks may improve our understanding of elemental and functional group incorporation into NOM.



Cosmogenic nuclide measurements of Pleistocene glacial erosion

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Glacial erosion plays a crucial role in landscape evolution at high altitudes and high latitudes, at the nexus between mountain building, surface processes and climate. Yet we lack a quantitative basis for incorporating glacial erosion into numerical models of these processes, and have few specific estimates of glacial erosion over 10^5 - 10^6 year timescales. We have developed a method of measuring past glacial erosion rates using cosmogenic nuclide depth profiles in bedrock. We are using this to determine glacial erosion histories, improve glacial erosion laws, and incorporate these into geomorphic process models.

Cosmogenic nuclide measurements on rock and soil surface samples have been widely used to estimate erosion rates in continuously exposed landscapes. Conversely, measurements on glaciated bedrock have been used primarily to date ice retreat, or, where such ages are compromised by prior exposure, to identify the sites as areas of limited glacial erosion. However, because the survival of nuclides produced beneath glaciated surfaces depends on subsequent glacial erosion, depth profiles accumulate information about the cumulative erosion history. Nuclide concentrations, concentration gradients and ratios are all sensitive to the history of exposure and erosion; we can use inverse methods to recover long-term average erosion rates of glaciated landforms from these data. Published cosmogenic nuclide measurements from glaciated bedrock surfaces suggest that these methods will be widely applicable to the study of mid- to late-Pleistocene erosion beneath glaciers and ice sheets.