(which initiate sedimentation) and their reversals (*r*). Formation of particulate metals (*p*) can proceed by (microbially mediated oxidation) oxidation (Fe(II) → $Fe(OH)_{3(s)}$, Mn(II) → $MnOOH_{(s)}$), by incorporation into the biomass and by adsorption at inorganic particulates ($Fe(OH)_{3(s)}$, $MnOOH_{(s)}$, clay minerals). The actual extent of these reactions is dependent on the solution parameters (pH, pE, presence of ligands) *i.e.* the *chemical speciation of the metal in the aquatic environment.* Resolubilisation is caused by low redox potential ($Fe(OH)_{3(s)}$ → Fe(II), $MnOOH_{(s)}$ → Mn(II)), by oxidation of the biological carrier and by desorption from inorganic particulate favored by low pH-values. In addition, metals such as Hg, Sn, Pb and Tl can be remobilized by biomethylation. The usual (biologically induced) distribution of pE and pH favors *p* over *r* near the surface and *r* over *p* near the bottom of the aquatic system. The resulting concentration gradients result in eddy-assisted back diffusion.

The marked increase in metal pollution (as documented by sedimentary record) gives rise to increasing concern for the *impact of metal ions upon the aquatic biosphere.* It is usually assumed that (some) metal ions are limiting at low concentrations and that most are toxic at higher concentrations. The sensitivity towards a given metal is largely dependent on the biological species. It is also generally agreed that availability of dissolved metals for phytoplankton is restricted to aquo ions. Hence, the biological impact of a given metal is again dependent on its chemical speciation. The situation is further complicated by the fact that some algae are able to release organic ligands (ferrichromes). Recent field studies seem to indicate that increase in metal concentration does not basically change the total amount of biota in a given aquatic system; the biological speciation is, however, greatly changed.

B34

The Electronic Structure of Iron Complexes of Bleomycin

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Bleomycin (BLM), a glycopeptide antibiotic, is activated in an Fe-dependent reaction and, when O_2 is present, catalyzes the cleavage of DNA. Drug activation takes place via two pathways. In the first, Fe(II)-BLM, an S = 2 species, and O_2 react to form a diamagnetic, ternary complex, 'oxygenated bleomycin'. The quadrupole splitting and isomer shift (ΔEq = 2.96 mm/sec, δ = 0.16 mm/sec) are suggestive of an electronic structure best described as low spin ferric bound to superoxide anion. Single electron reduction of oxygenated bleomycin yields 'activated bleomycin', a form of the drug that is kinetically competent to cleave DNA. As a second pathway for activation, Fe(III)-BLM reacts with peroxide; Fe(II)-BLM is not produced as an intermediate.

Activated bleomycin is an S = ½ species with a well resolved EPR spectrum (g = 2.26, 2.17, 1.94). When prepared with ^{57}Fe, the g = 1.94 EPR feature is split by 22 gauss, demonstrating that the electron spin resides primarily on the iron. When activated bleomycin is prepared from Fe(II)-BLM and $^{17}O_2$, the EPR spectrum is broadened, demonstrating the presence of at least a single oxygen atom derived from O_2.

Concomitant with DNA cleavage, activated bleomycin decomposes to form Fe(III)-BLM, an S = ½ species with EPR features (g = 2.45, 2.18, 1.89) and Mössbauer parameters (ΔEq = 2.85 mm/sec and δ = 0.20 mm/sec) closely resembling those of cytochrome P-450. Fe(III)-BLM, in the presence of phosphate or arsenate, or at pH below 4.5, becomes high spin with g_{eff} = 4.3 at 77 °K (E/D ~ 0.3). Yet, Fe(III) remains bound to the drug.

The bonding of iron to BLM is affected by the presence of DNA. Changes are observed in the g = 1.94 EPR feature for the activated complex, and in the hyperfine interaction with ^{14}N in the low spin ferric complex, as determined from differences in the electron spin echo spectrum. DNA also prevents the conversion of the iron in the low spin ferric complex to an S = 5/2 species by phosphate or arsenate.

B35

Chemical Aspects of Structure, Function and Evolution of Superoxide Dismutases

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The superoxide dismutases (SOD) constitute a class of metalloproteins having either Cu/Zn, Mn or Fe as their prosthetic group and their function is to dismute O_2^- to H_2O_2 and O_2. The distribution of the SODs has to be considered in the light of the acquisition of a permanent defence by organisms against any form of toxicity arising from the increase, by photosynthetic organisms, at atmospheric oxygen. Anaerobic sulphate reducing bacteria and fermenta-