

Redox-dependent phosphorus burial and regeneration in Cretaceous black shales and Mediterranean sapropel S5

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Phosphorus (P) is a key nutrient and its availability can limit marine primary productivity. The efficiency of marine P burial is strongly dependent on the oxygenation state of bottom waters. The feedbacks between P availability, primary productivity, oxygen depletion and P regeneration from marine sediments may have played a crucial role in initiating and/or sustaining periods of high marine primary productivity and organic carbon burial in Earth's history.

Two type examples of organic-rich (organic carbon (OC) > 1%) sediments from such periods are the black shales deposited during oceanic anoxic event 2 (OAE 2, 93.5 Ma), and the Eastern Mediterranean sapropel S5 (~125 ka). In both sediments, enhanced OC/total P ratios indicate enhanced release of P from organic matter with negligible 'sink-switching' to authigenic P-containing minerals. Clear differences in P cycling are observed for the two sediment types, however, attributable to varying degrees of oxygen depletion in the water column. Phosphorus burial nearly shut down in OAE 2 black shales under severe euxinia (ODP Leg 207, site 1260) while it increased during formation of sapropel S5. This increase is likely the result of enhanced preservation of fish debris.

Our results show that local conditions such as the degree of (bottom water) oxygen depletion affect not only the efficiency of P burial, but also the relative importance of the various P phases. In particular, biogenic Ca-P (fish debris) can become a major burial sink for P under anoxia.

Iron oxide photodissolution in the presence of siderophores

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Iron is an essential nutrient for almost all known organisms and its low bioavailability limits primary productivity in large scale ecosystems. High affinity iron acquisition mechanisms involving the synthesis and exudation of iron specific ligands (siderophores) are widespread among prokaryotic microorganisms. Marine phytoplankton that is responsible for much of the marine primary productivity does not exude siderophores and is not efficiently taking up iron-siderophore complexes. However, previous work has shown that sunlight also promotes iron oxide dissolution by a photoreductive dissolution mechanism. This process generates siderophore photoproducts and transient reduced iron species, potentially increasing iron bioavailability to phytoplankton in the photic zone. In this presentation we will discuss mechanistic aspects of this ecologically important process in terms of the siderophore speciation at the mineral surface as measured by IR-spectroscopy and of its reactivity as inferred by measurements of the reaction rates.

Release of Fe(II) from lepidocrocite irradiated with simulated sunlight but in the absence of organic ligands was observed in control experiments. We conclude that intrinsic photochemical processes at the mineral surface lead to reductive dissolution of the mineral. A further increase of dissolution rates of irradiated suspensions was observed in the presence of DFOB, a trihydroxamate siderophore that forms non-photoreactive complexes in solution. Similar effects were observed in the presence of aerobactin, a siderophore possessing an alpha hydroxy carboxylate functional group. Comparison with citrate suggest that ligand to metal charge transfer is not a dominant photodissolution process in the presence of aerobactin. Alternative mechanisms by which siderophores promote lepidocrocite photodissolution are discussed.