

The Impact of Light on Iron Biogeochemistry in Sediments

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Photochemical reactions play an important role for iron bioavailability in natural waters. However, the impact of light on biogeochemical iron cycling in sediments is poorly understood. It is well recognized that light may drive microbial phototrophic iron(II) (Fe(II)) oxidation, but other mechanisms, including the photoreduction of organically complexed ferric iron (Fe(III)), may take place in sunlit sediments. We suggest that Fe(III) photoreduction can produce substantial amounts of dissolved Fe(II) in the top sunlit sediment layers, even in the presence of oxygen. Photoproduced dissolved Fe(II) (Fe²⁺) constitutes a so far overlooked source of substrate for microbial Fe(II) oxidation in sunlit sediments shaping the sedimentary microbial community. Fast photochemical Fe(II) production and concurrent microbial and chemical Fe(II) oxidation lead to a cryptic reaction network where the individual opposed processes are difficult to detect with analytical tools. In order to determine the impact of light on iron biogeochemistry, marine and freshwater sediment cores were incubated under light and dark conditions and physico-chemical parameters (Fe²⁺, O₂, dissolved S-species) were quantified with microsensors at high spatial and temporal resolution. We observed that illumination led to elevated Fe²⁺ concentrations (up to 100 µM) in the top 0-5 mm of the sediment. Organic-rich marine sediments suffered from fast Fe²⁺ depletion down along the redox gradient, when exposed to light. Our experiments showed that this depletion cannot be caused simply by diffusion or chemical oxidation. In recent experiments we could narrow down this light-dependent Fe²⁺ depletion to microbial activity, potentially involving cable bacteria.

Our findings highlight that previous knowledge on the impact of light on the biogeochemical iron cycle in sediments is incomplete and that our understanding of potential Fe²⁺ sources and sinks needs to be revised. We detected so far overlooked light-driven biogeochemical mechanisms that strongly impact the Fe²⁺ availability in marine and freshwater sediments.