

Formation of layered Fe(II)-Al(III) hydroxides during reaction of Fe(II) with γ -Al₂O₃ and montmorillonite

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The biogeochemical cycling of iron in aqueous geochemical environments is intimately linked to the cycling of carbon, nitrogen, phosphorus and sulfur, and strongly impacts the solubility and speciation of trace metal and metalloids in these systems. In riparian zones, reductive dissolution of Fe(III)-(oxyhydr)oxides mediated by soil microbes leads to a buildup of high concentrations of dissolved Fe(II) in soil solution and concurrent release of sorbed contaminants. The fate of released Fe(II) is at least partially controlled by sorptive interactions with Al-oxides and phyllosilicates minerals in the soil matrix. Here, X-ray absorption spectroscopic evidence is presented for the formation of Fe(II)-Al(III)-layered double hydroxide phases during reaction of Fe(II) with Al-oxide and montmorillonite clay. These phases form fast (on time scales < 24 h) and are therefore expected to be a major sink for Fe(II) released during reductive dissolution of Fe(III)-oxides. In addition, owing to small particle size, layered structure, and high Fe(II) content, these phases are likely to be highly reactive towards redox-active contaminants such as Cr(VI), and may control retention of divalent metals such as Ni(II) and Zn(II) through adsorption and coprecipitation reactions. The research presented here characterizes formation of these phases in relation to observed macroscopic uptake trends of Fe(II) as a function of Fe(II) concentration, pH and reaction time.

Cycling of nitrogen in the Namibian coastal upwelling system – The stable isotope view

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Nitrogen is a key element in regulating biological processes in the ocean, and the history of the nitrogen cycle under past conditions on Earth is of high relevance for paleoceanographic and paleoclimate studies. The ratio of the two stable N-isotopes (¹⁵N/¹⁴N; expressed as $\delta^{15}\text{N}$ versus air N₂) preserved in sediments is commonly assumed to reflect the isotopic composition of N-sources, or the extent of assimilation by phytoplankton. But although $\delta^{15}\text{N}$ is widely appreciated as one of few available proxies to reconstruct marine nutrient cycles in the geological past, there are several biases on the $\delta^{15}\text{N}$ of sedimentary records. Here we explore the dynamics of nitrogen isotopic composition in several compartments of reactive nitrogen in a depositional setting characterized by extreme gradients in $\delta^{15}\text{N}$ of nitrate, suspended matter and surface sediments – the coastal upwelling area offshore Namibia. The gradient observed in $\delta^{15}\text{N}$ of surface sediments mirrors the state of oxygen depletion in the water in contact with sediments, as well as changes in source nitrate, in water-column denitrification, in particle advection along the shelf break, and in dominant upwelling mode (coastal versus shelf break upwelling). Based on data of nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in several seasonal sampling campaigns, we attempt to isolate possible diagenetic effects by determining $\delta^{15}\text{N}$ of suspensions and surface sediments in conjunction with indicators of organic matter quality (i.e., the degradation index of amino acids, C-normalized amino acid concentrations) in the pronounced oxygen gradient of the region. Besides sharpening the $\delta^{15}\text{N}$ as a proxy for the geological past, the data also allow us to examine some basic biogeochemical concepts underlying nutrient stoichiometry in the ocean. This is important in light of the expected increasing importance of upwelling processes for the supply of nutrients to the surface ocean.