## Iron cycling in freshwater environments - A theoretical concept on the dynamics of coupled chemical an biological iron redox processes

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Iron represents one of the most abundant redox-active elements in near surface aqueous environments where it plays a key role in several biogeochemical processes. Although, the conversion of iron(II) and iron(III) under various physicochemical conditions has been described frequently, the linkage and competition between biotic and abiotic oxidation, reduction, dissolution- and precipitation mechanisms have not yet been investigated. One of the remaining questions is how the geochemical iron cycle functions and varies in an ecosystem that shows dynamic chemical conditions (i.e. oxicanoxic, pH changes, light conditions). For this purpose a conceptual study is proposed to evaluate how the physicochemical gradients develop in the sediment matrix, and how this affects the dominance of either oxidative or reductive processes. Under consideration of thermodynamic and kinetic aspects the availability of substrates and the development of different iron-depending microbes will be estimated. Accounting for characteristic chemical conditions the dimension and overlap of microbial habitats and chemically dominated zones will be assessed. This approach is expected to provide information about the structure of the redox zone and the occurrence of geochemical niches in which specific microbes may flourish. External factors, such as light intensity or seasonality will be included and the effect on the spatial variability of microenvironments will be evaluated. The concept will firstly be based on literature data from a freshwater environment, and be validated at a later step with high resolution field data from a freshwater lake sediment (Lake Constance, Germany).

## Rare earth element distribution and temporal variability in supercritical vapor phase fluids from 5°S, MAR

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Hydrothermal fluids obtained between 2005 and 2008 from two vent fields at 5°S, Mid-Atlantic Ridge display a strong temporal variability of their rare earth element (REE) distribution. This variability is independent of the major element composition of the fluids being stable since 2005 and has been observed at different time scales of minutes to years. Fluids venting at Turtle Pits and Comfortless Cove represent vapour phase fluids emanating at conditions above the critical point of seawater (407°C, 298 bars), influenced by a recent magmatic event in 2002. The chondrite-normalized REE distribution, formerly thought to be relatively uniform at submarine hydrothermal vent systems along mid-ocean ridges, varies between the typical light REE enrichment accompanied by positive Eu anomalies relative to the heavy REE (type I) and strongly enriched REE concentrations with a concave downward distribution with a maximum enrichment of Sm and weakly positive or even negative Eu anomalies (type II). Besides the temporal changes in REE distribution and concentration, we observed a strong variability in fluid flow, with vigorous to weak venting, clogged and newly formed vent orifices within days and changing fluid temperatures within minutes.

As indicated from a positive correlation of the concentrations of REE, Ca and Sr, the formation of hydrothermal anhydrite plays a major role with respect to the REE distribution at 5°S vent fluids. We will demonstrate that anhydrite precipitation/dissolution controls the transformation of one fluid type to the other, thereby changing the total REE concentrations as well as  $Ce_{CN}/Nd_{CN}$  and the size of the Eu anomaly in solution, and discuss the formation of a primary reaction zone fluid as possibly represented by fluid type II. Similar fluids might be common during the evolution of other hydrothermal systems as well, but there REE signature has later been modified during fluid migration controlled by the transport capacity of the solution and sorption/incorporation onto/into secondary minerals.