

## Geo-Bio interactions in shallow water hydrothermal vents and their impact on trace metals

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Life at shallow- and deep-sea hydrothermal vents is exposed to high concentrations of different metals in the venting fluids. Some are biologically essential and serve as micronutrients (e.g. iron), while others act toxic at even low quantities (e.g. copper).

Hydrothermal vents at the sea floor release large volumes of these metal rich fluids into the ocean. Several studies confirmed that microorganisms, living at these habitats, produce small molecules, organic ligands that are able to form strong complexes with different metals to enhance its bioavailability or to reduce its toxicity. Due to the formation of metal-ligand complexes, keeping the metals soluble, the trace metal flux into the ocean is expected to be higher than assumed until recently. While deep-sea vents have been intensively studied with respect to metal complexation, corresponding knowledge about shallow-marine vents is rather rare.

In this study, we want to examine the total dissolved Cu and Fe concentrations, as well as corresponding Cu- and Fe-binding ligand concentrations at shallow water hydrothermal vent fields by a voltammetric ligand titration, using adsorptive cathodic stripping voltammetry. Hydrothermal fluid and pore water samples were taken off the coast of Milos, Greece (2012) and in the shallow waters off Dominica, Caribbean (2013). A third set of samples will be collected during a SONNE cruise in June/July 2013 at the Coriolis Troughs, Vanuatu.

As an outcome, a complex data set on the complexation of Fe and Cu at shallow-marine hydrothermal systems, which are not only influenced by chemoautotrophic organisms, as at deep-sea vents, but also by phototrophic microbes, is aimed. Parameters such as total concentrations of dissolved Fe and Cu, as well as the quantification of ligands and determination of stability constants will give a detailed overview on the geo-bio interactions happening at hydrothermal systems in shallower water depths and to what extent they influence the metal flux into the ocean.

Uncertainties within this research project might start with the sample treatment. To avoid changes, such as metal precipitation or ongoing complexation processes, all aqueous samples are directly filtered and frozen at -20°C. This is the common treatment for such investigations, however, one never knows if all processes within the solution really stop and if the geochemistry stays the same, until the samples are being measured.

Secondly, as every method, also the voltammetric measurements display uncertainties with respect to analytical errors during each run. Additionally, the addition of buffer solutions, standards and artificial ligands increases the risk of contamination.

Another uncertainty within my research is the representativeness of the samples investigated. The amount of samples taken at each shallow marine hydrothermal vent site is limited due to sampling constraints and maybe too low to project the geochemical and biological results of each individual realm to the whole system.

However, this project is the first study on organic metal complexation processes at shallow marine hydrothermal vents and will therefore serve as an essential basis for ongoing research at these habitats in the future.