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REY distribution and concentration in bottom seawater and oxic pore water in the CCZ, NE Pacific: pilot study on the application of a DGT passive sampling method in deep sea environments

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Sampling and analysis of trace elements in open seawater and in sediment pore water in the deep sea is challenging due to small sample volumes and matrix effects. Here we evaluate an alternative method using the technique of diffusive gradients in thin films (DGT passive samplers), focussing on rare earth elements and yttrium (REY). DGT measures the labile fraction of metals in situ by fixing them on a Chelex resin after diffusion through a gel layer, providing a diffusive flux and averaged in situ concentrations of elements during the time of deployment. As the accumulated element concentrations increase with exposure time to solution, long-term deployment times overcome low trace metal concentrations in seawater and pore water. So far, no deep-sea applications of passive samplers are yet reported.

Sampling was performed in bottom seawater and surface sediments in the German licence area for manganese nodule exploration in the Clarion Clipperton Zone (CCZ, research cruise SO268 in April/May 2019), deployment times ranged from 12 hours in sediments to 4 weeks in open seawater.

Seawater DGT's were deployed 0.5 m to 8 m above the seafloor. PAAS-normalized REY show the typical seawater pattern, with increase from LREE to HREE, a strong negative Ce anomaly, a kink from Gd to Tb, and a pronounced positive Y/Ho anomaly. The pattern and calculated concentrations agree very well with reported dissolved REY (<0.2 μm) for Pacific deep water (Alibo and Nozaki, 1999). Sediment DGT sticks were deployed in cores taken with a multicorer and cover the first 15 cm of the sediment. They provide in situ high-resolution profiles of trace metal fluxes and were analysed in 0.5 cm to 2 cm segments. We observe smooth PAAS-normalized patterns with negative Ce anomaly, an increase from LREE to MREE, and a slight decrease from Tb to Lu, sometimes accompanied by a small positive Y/Ho anomaly. The calculated concentrations generally increase with depth. Paul et al (2019) previously described very similar distribution patterns for CCZ sediment pore water and suggested Mn and Fe phases as the REY source. The pore water REY patterns clearly differ from bottom seawater already in the first centimetres of surface sediment- this sharp shift demonstrates that the dissolved pore water REY pool in the sediment surface is controlled by fluid-mineral equilibria.

The DGT passive sampling method may provide an additional tool to investigate biogeochemical processes at the deep-sea sediment-water interface and in the open ocean, and to monitor effects of anthropogenic disturbances at the seafloor on benthic trace element fluxes. We will discuss uncertainties of concentration calculation resulting from diffusion coefficients and from non-steady state conditions in pore water, and the comparability of DGT-derived distribution pattern and concentrations with results from physically filtered water. The DGT labile fraction is thought to represent the bioavailable fraction of trace elements and may also include colloids and nanoparticles (NPCs).

Alibo and Nozaki, 1999: *Geochimica et Cosmochimica Acta* 63, pp. 363-372.

Paul et al, 2019: *Geochimica et Cosmochimica Acta* 251, pp. 56-72.