Metal-rich brown layers in Arctic Ocean sediments: Climate versus diagenesis

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The sediments of the central Arctic Ocean are a unique archive for past climate and environmental changes in this highly sensitive ocean region. Amongst the most prominent and widespread features of Arctic Quaternary deposits are marked cm- to dm-thick brown layers. Their origin is unclear, and might either be related to specific environmental conditions during either deposition, or to diagenesis. To understand the genesis and composition of these layers, we studied sediments cores from the southern Mendeleev Ridge (RV *Polarstern* Expedition ARK-XXIII/3) by inorganic-geochemical methods (XRF, ICP-MS, Fe extraction) at high resolution.

The brown layers are consistently enriched in Mn and Fe (oxyhydr)oxides, but also in various trace metals (As, Co, Cu, Mo, Ni) that most probably adsorbed to Mn and Fe phases and were scavenged from the water column. These metal enrichments are likely related to enhanced riverine input to the Arctic Ocean, as Arctic river waters are known to be metal-rich. Increased fluvial runoff should be related to a more intense hydrological cycle under warmer (interglacial-type) climate conditions.

However, pore water data indicate ongoing Mn (but not Fe) diagenesis in the recovered sediments, questioning the primary nature of the observed metal enrichments. We suggest that relative changes in the enrichment patterns of specific trace metals (especially of Co and Mo) in individual brown layers might be used to determine if the composition of the respective layers was overprinted by diagenetic processes.

In detail, we observe that brown layers currently serving as pore water Mn sources have Co/Mo ratios above 5, while those layers acting as pore water Mn sinks have Co/Mo ratios below 5. This trace metal pattern may be explained by preferential retention of Co in dissolving Mn (oxyhydr)oxide layers. In contrast, Mo is preferentially desorbed, diffuses through the pore space in conjunction with Mn, and re-adsorbs onto freshly precipitating, authigenic Mn (oxyhydr)oxides. However, the wider application of trace metal ratios as 'diagenetic markers' in Arctic sediments requires further investigation.

Nitrate reduction drives distant sulfide oxidation

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Recent observations in marine sediments show that electric currents may couple oxygen reduction at the sediments surface to sulfide oxidation deep within the sediment [1]. In this study we tested if electric currents can couple also nitrate reduction to sulfide oxidation

Sediment collected from Aarhus bay (Denmark) was pre-incubated for 2 months in two different aquaria: one with oxic seawater and another where oxygen was replaced with nitrate. After the pre-incubation, sulfide, oxygen and pH distribution in the sediment were determined with microsensors whilst a biomicrosensor was used to measure nitrate & nitrite.

Our concentration profiles showed a 4 mm separation between nitrate and sulfide in sediments incubated with nitrate in the water column. In sediments incubated with oxygen in the water column, oxygen and sulfide were separated by 25 mm. In both types of incubation, the pH signature indicated the presence of electric currents coupling spatially segregated biogeochemical processes.

These results provide an important indication of the capacity of nitrate to sustain sulfide depletion over distances not coverable by diffusion only. Moreover demonstrating that oxygen is not the only electron acceptor able to sustain such a system, implies that this distant coupling can be more spread in nature than previously expected.

[1] Nielsen *et al*. (2010) *Nature* **463**, 1071-1074.