4.1.P07

Organic sulfur in Namibian shelf sediments – rates and processes

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Organic sulfur compounds (OSC) are formed under anoxic and iron-limiting conditions in sediments with high concentrations of organic matter (OM) and bacterial sulfate reduction as the dominant anaerobic carbon mineralisation pathway. Sulfide evolving from that process as well as other reduced sulfur compounds, e.g. polysulfides and polythionates, may now react with the OM to form OSC via crosslinking of small organic molecules. Crosslinked OSC have been suggested to be more refractory. Thus, the formation of OSC acts as a sink for sulfide and enhances carbon preservation. The absence of reactive iron is crucial for that process, since it would react with sulfide to form iron monosulfide and pyrite, and compete successfully with the formation of OSC.

Although specific molecular OSC-forming reactions have been described, direct formation rates have not been determined. To improve our understanding of OSC-formation, we analyzed two sediment cores of sulfidic organic-rich sediments from the Namibian coastal upwelling region. A budget of different reduced sulfur species (elemental sulfur (S^0), iron monosulfides (FeS), pyrite sulfur (FeS_2) and OSC) was compiled using a sequential methanol-HCl-Cr(II)HCl-extraction. In addition, available reactive iron was determined by means of sodium dithionite extraction. Finally, bulk formation rates were determined by ^{35}S radioisotope labeling. Sulfide produced by sulfate-reducing bacteria is subsequently incorporated into the different sulfur species and measured using liquid scintillation counting.

Sodium dithionite-leachable iron indicated extremely low concentrations of reactive iron. A mass budget of the organic and inorganic sulfur species demonstrated the importance of OSC-formation in the Namibian shelf sediments. OSC were the second most abundant sulfide-containing group, and contributed ~40% to the total sulfur pool. In a 6 m-long gravity core, no change in the ratio of OM to OSC was observed suggesting that the rates of formation for most OSC are very fast and nearly completed in the uppermost 30 cm. We will report on the radiotracer experiments to quantify the specfic rates of individual sulfur species groups.

4.1.P08

Reactivity of organic matter in Benguela & Arctic sediments: The role of supply vs. quality

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Total organic carbon turnover in sediments is controlled by the quantity and quality of exported Particulate Organic Material (POM) and its compound-specific degradation dynamics. As exported organic carbon is subject to both, water column and early diagenetic alteration processes distinct molecular changes imply a reduction of POM reactivity and bioavailability.

We applied molecular degradation indices such as the Chlorin Index (CI) [1] and the Amino Acid Index [2] and compared them to overall organic carbon turnover. Molecular degradation indices provide compound-specific information of organic carbon quantity and the relevance of quality. Chlorins are a collection of intact chlorphylls (chla,b,c), its degradation products and pigments containing the "chlorin-ring-system". Total chlorins are a measure of the supplied organic matter whereas the CI characterizes organic carbon quality, freshness and reactivity. The CI is defined as 0 for highly reactive carbon up to 1 for reworked matter. The Amino Acid Index is a protein based indicator linking organic carbon bioavailability to its degradation dynamics [2].

The organic carbon turnover as measured by Total Oxygen Uptake (TOU) and Sulfate Reduction Rates (SRR) was compared directly to degradation indices and parameters of total organic matter supply (Total Chlorins, TOC) in the Benguela Upwelling Slope sediment. A regionally uniform CI of 0.8 and high total chlorin contents in these sediments, suggests that the central part of the Benguela Upwelling acts as a depot center of altered sediment. Enhanced areal SRR and TOU as a response to high carbon amounts support the hypothesis that large quantities of low grade organic matter drive local turnover. In contrast, Arctic sediments show a strong correlation between OM quality and reactivity as measured by medium quantities of highly reactive organic carbon (CI 0.3-0.4). A fraction of the organic carbon exhibits immediate mineralization within the upper sediment layer as shown in intensely shifting CI depth profiles (0.3-1) and depth-related increasing respiration rates with SRR contributing 50% to organic carbon degradation.

References

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