

## A multi-component reactive transport model assessment of microbial processes and trace metal cycling across a gradient in sulfate reduction rates along the California Margin

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Sediments and pore water from 4 ODP Leg 167 sites along the California Margin (1011, 1017, 1018 and 1020) were used to compare biogeochemical processes across a gradient of sulfate reduction (SR) rates with the purpose of studying the processes that control these rates and how they affect trace metal redistribution. Measurements of the trace element composition of pore water and sediment along with %CaCO<sub>3</sub>, %biogenic silica, wt% carbon and δ<sup>13</sup>C of Total Organic Carbon (TOC) were used to constrain the multicomponent reactive transport model CrunchFlow. The rates of sulfate reduction, methanogenesis and anaerobic methane oxygenation (AMO) were constrained by fitting the model to the measured concentration profiles. The sites are distinguished by the depth of AMO: a shallow zone is observed at sites 1018 (14 to 19 mcd) and 1017 (23 to 27 mcd), while deeper zones occur at sites 1011 (45 to 55 mcd) and 1020 (97 to 113 mcd). In general, the sulfate reduction rates are faster (on the order of 9-9.9\*10<sup>-17</sup> mol/L/yr) for the shallow zones, compared to 1-1.4\*10<sup>-17</sup> mol/L/yr for the deeper zones. AMO rates are also faster at the shallow belt 2\*10<sup>-7</sup> mol/L/yr compared to 3\*10<sup>-8</sup> mol/L/yr at the deeper sites. Sites with shallow sulfate reduction zones appear to have high rates of AMO resulting in high alkalinity concentrations close to the sediment-water interface. The dissolved metal ion concentrations also varied between the sites, with Fe (0.01-7μM) and Mn (0.01-57μM) concentrations highest at Site 1020 (water depth 3000m) and lowest at site 1017 (water depth 950m). The highest Fe and Mn concentrations occurred at various depths, with no direct correlation to sulfate reduction and alkalinity maximum values. Modeling of the dissolved and solid SiO<sub>2</sub>, Ca, Mg, K, Mn and Fe is used to establish the relationship between the biogeochemical reactions and trace metal variations and to better constrain the parameters that influence the trace metal distributions in the sediment column.

## Dissolved reactive manganese at pelagic redoxclines

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Experiments with suboxic freshwater and seawater suggest a dissolved reactive manganese fraction (dMn<sub>react</sub>) that completely oxidizes within 36 h, mainly by microbial activity. The fast redox cycle of Mn drives the 'Mn pump' transporting metals into anoxic basins. A difference method can be used to determine dMn<sub>react</sub>. One aliquot of a water sample is directly filtered and represents the total dissolved Mn. A second aliquot is aged under atmospheric oxygen and app. 20°C and filtered after 36 h representing the residual dissolved Mn(II). The concentration of dMn<sub>react</sub> is calculated as difference of both aliquots.

Application to the Black Sea revealed dMn<sub>react</sub> profiles comparable to published Mn(III) patterns analysed with a polarographic method. Both methods show that the upper part of the suboxic zone consists exclusively of dMn<sub>react</sub> or Mn(III). dMn<sub>react</sub> is a half quantitative measure of dissolved Mn(III). An unknown fraction of i) autocatalytic oxidation of dissolved Mn(II) by readily produced MnO<sub>x</sub> and ii) microbial Mn(II) oxidation. Thus, the present method helps to assess the full potential for oxidation of dissolved Mn within an aquatic environment. The method has the advantage that sample preparation can be easily done on site, followed by analysis of dissolved Mn by conventional methods in the lab.

dMn<sub>react</sub> was also detected in the Landsort Deep (Baltic Sea) with values distinctly increasing from the outer regions towards the central part (max. 3 μM). Similar to the Black Sea, dMn<sub>react</sub> concentrations increase in the suboxic transition zone separating oxygenated and H<sub>2</sub>S containing waters. In contrast, almost no dMn<sub>react</sub> was present in the Gotland Basin (Baltic Sea). Pronounced lateral currents and turbulence in the Gotland Basin prevent the formation of a stable suboxic zone, a prerequisite necessary for accumulation of dMn<sub>react</sub>. Such intrusions supply trace amounts of O<sub>2</sub> and H<sub>2</sub>S thus causing either immediate oxidation/reduction of dMn<sub>react</sub> or deterioration of its stabilising ligands.

Analysis of dMn<sub>react</sub> in the seasonally anoxic Lake Dagow (Germany) revealed maximal concentration of 6 μM. This value significantly exceeds the level of the Landsort Deep most likely due to the stable stratification of this lake during sampling.