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Reactive-transport modelling of stable sulphur isotope distributions in surface sediments of the Benguela upwelling system (Namibian shelf)

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A reaction-transport model (RTM) has been applied to a data set collected from anoxic marine sediments on the Namibian shelf. This region is among the most biologically productive marine systems in the world, and phytodetritus deposited on the sea bed results in widespread shelf anoxia and intense rates of sulphate reduction in surface sediments (>100 mM/y). Strikingly, however, sulphide concentrations in the top 6 cm below the sediment-water interface are low (0.02mM). This is believed to reflect the intense bacterial oxidation of hydrogen sulphide by abundant sulphide-oxidizing bacteria *Thiomargarita namibiensis* and *Beggiatoa* sp using nitrate as the electron acceptor. However, the rates and fractionation ($\varepsilon_{H2S-SO4}$) of this pathway have never been determined experimentally. In this study, the RTM was used to unravel the rates of sulphate and sulphide turnover by tuning the model to depth distributions of pore water sulphate and sulphide concentrations and stable sulphur isotope (^{32}S and ^{34}S) distributions. The fractionation ($\varepsilon_{H2S-SO4}$) of sulphide oxidation with nitrate was determined to be around 30‰ and compares to a fractionation during sulphate reduction ($\varepsilon_{SO4-H2S}$) of around 85‰. This is one of the highest fractionations reported in the literature for sulphate reduction and is far higher than values obtained experimentally by pure cultures of sulphate reducing bacteria (40-50‰).