Identification and quantification of redox reactions at the sea water-brine interface of the Orca Basin (Gulf of Mexico)

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The Orca basin is a depression located on the northern slope of the Gulf of Mexico. It drops from the surrounding seafloor water depth (1800 m) to about 2400 m. The lower 150 m of the basin are filled with a brine which is separated from the overlying sea water by a strong density stratification due to the increase of salinity from 35 to about 260‰.

The stratification lowers transport rates dramatically, hence, increasing the residence time of settling particulate organic matter in the salinity transition zone. Furthermore, resupply of oxygen to this zone is limited. As a result, the oxic-anoxic interface coincides with the salinity transition zone, promoting anaerobic degradation processes, as well as redox reactions involving reduced byproducts of anaerobic degradation such as Mn(II), Fe(II) or sulphide. The depth range over which these reactions occur extends over several meters, instead of the centimeter scale redox gradients usually observed in sediments.

Identification of reaction pathways

During three cruises, profiles of conductivity, alkalinity, pH, O_2, dissolved Fe(II) and Mn(II), total dissolved sulphide, NO_3^-, NH_4^+, particulate Mn and Fe were measured. Colony forming units of bacteria with Mn(IV) and Fe(III) as terminal electron acceptor, and Mn(II) and Fe(II) as terminal electron donor were also counted (Van Cappellen *et al.*, submitted, Environ. Sci. Technol.).

In order to determine the salinity range of production or consumption of solute species mixing diagrams are used. In this method, solute concentrations are plotted against salinity, hence, eliminating the effects of variable transport intensities with depth. Additionally, alkalinity is used as an indicator of organic degradation pathways (Stumm and Morgan, 1996). Bacterial counts further constrain the spatial distribution of microbially mediated redox reactions.

The results of this qualitative analysis show that redox cycling of Mn dominates the geochemistry and microbiology in the salinity transition zone. Observed high levels of dissolved Mn are mainly due to dissimilatory Mn oxide reduction. Reduction of Mn oxides by reduced inorganic species, such as H_2S, Fe(II) or NH_3, only accounts for a minor fraction of the observed production of Mn^{2+}. In the uppermost part of the transition zone, Mn oxygenation takes place. High numbers of colony forming units of Mn oxidizers in this depth range indicate that this reaction is microbially mediated. A small fraction of Mn is permanently removed from the transition zone by precipitation of $MnCO_3$.

Fe(III) mostly reacts with sulphide and does not contribute significantly as an electron acceptor for the degradation of organic matter. Sulphate reduction dominates in the brine (Van Cappellen *et al.*, submitted, Environ. Sci. Technol.).

The proposed set of dominant reactions with increasing depth in the salinity transition zone (2180 m to 2280 m) is:

$$Mn^{2+} + 0.5O_2 + H_2O \rightarrow MnO_2 + 2H^+$$

$$MnO_2 + 0.5CH_2O + 1.5H^+ \rightarrow Mn^{2+} + 0.5HCO_3^- + H_2O$$

$$MnO_2 + H_2S + 2H^+ \rightarrow Mn^{2+} + 2H_2O + S^0$$

$$MnO_2 + 2Fe^{2+} + 4H_2O \rightarrow 2Fe(OH)_3(s) + Mn^{2+} + 2H^+$$

$$Mn^{2+} + HCO_3^- \rightarrow MnCO_3(s) + H^+$$

$$2Fe(OH)_3(s) + 3H_2S \rightarrow 2FeS + S^0 + 6H_2O$$

Inverse modelling approach

An inverse modelling approach is applied to calculate depth distributions of net rates of production and consumption of dissolved species. The goal of this approach is to find the rate distributions which best explain the measured concentration distributions.

Based on the available data, the possible occurrence of lateral intrusions and shear driven transport processes just above the brine can not yet be addressed conclusively. Hence, for simplicity, lateral transport is ignored and the model is formulated only in one dimension. Conservation of mass of a solute species, with transport by vertical turbulent diffusion, can be written as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(K_z \frac{\partial C}{\partial z}\right) + R$$

where C is the concentration, K_z is the apparent diffusion coefficient, and R is the net reaction rate. Data collected since the discovery of the basin in the '70s (Shokes *et al.*, 1977) show that the solute depth profiles have not changed appreciably (Trefry *et al.*, 1984; Van Cappellen *et al.*, submitted, *Environ. Sci. Technol.*). Therefore the conservation equations are solved at steady state.

Relative changes of the diffusion coefficient with depth are calculated from depth profiles of conservative tracers, namely salinity and temperature. Absolute values are constrained from heat flux data and from diffusion coefficients reported for the open ocean (Nihoul and Jamart, 1988). The distribution of K_z thus obtained agrees well with the assumption that molecular diffusion governs transport across the most stably stratified region between seawater and brine.

For the numerical calculations, a finite difference method is used, dividing the modeled depth range into n equally spaced boxes. Concentration depth profiles of each solute are computed based on the known K_z distribution, and an initial guess for the rate distribution. In an iterative process the latter is then systematically altered. The net rate distribution which best explains the measured concentrations, for a given number of boxes, is found by minimizing the deviation between calculated and measured concentrations. The procedure is then repeated, after reducing the number of boxes by one. By comparing the errors for the best rate distributions as a function of the numbers of boxes, it is possible to objectively determine the optimal number of boxes, in addition to the best rate distribution.

For the calculation of the deviation between measured and calculated concentrations, the traditional weighted least square approach is modified in order to implement geochemical constraints on the rates. These constraints allow us to include a priori knowledge in the minimization procedure. 'Penalty functions' are formulated in such a way that violating a geochemical constraint increases the calculated error drastically. An example of a constraint is that the net rate of oxygen must be negative below the euphotic zone, that is, O_2 can only be consumed. Formally, the error calculation can be expressed as:

$$\text{error} = \sum_{i=1}^{n}\left(w_i(C_{\text{meas},i} - C_{\text{calc},i}(K_{z,i}, R_i))^2 + P\right)$$

where w is the weighting factor, P is the penalty function, n is the number of boxes in the finite difference scheme, and C_{meas} and C_{calc} are the measured and calculated concentrations, respectively.

By comparing the relative rates of the different dissolved species of interest with the stoichiometries of the expected reactions, net rates can be separated into the contributions of different reactions, and the spatial distribution of those reactions can be determined. Furthermore, large differences between the idealized stoichiometries given previously and the stoichiometries inferred from the relative magnitude of rates may reveal the existence of additional reactions.

The advantage of inverse modelling, compared to a forward approach, is that the reactions are not imposed *a priori*. Thus our understanding of the system can be tested objectively by comparing the expected set of reactions to the modeled net rates of production and consumption of the various chemical species.

The inverse modelling work is currently being carried out. Preliminary results are consistent with an intense redox cycling of Mn in the transition zone between seawater and brine.

References

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