Mineralization pathways in the sediments of Lake Baikal – A microsensor and modeling study

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Burial of organic matter in Lake Baikal (Siberia, Russia), is strongly affected by the mineralization processes in the surface sediments. These processes were analyzed on-site using an array of ion-selective electrodes (O_2, pH, CO_3^{2-}, Ca^{2+}, NH_4^+ and NO_3^-) and a micromanipulator controlled by a laptop computer. The setup was used to measure concentration profiles at sub milimeter resolution immediately after retrieval of sediment cores from the South Basin (160m, 600m 700 m and 1400 m depth).

Modeled oxidation rates of organic carbon constrained by O_2 and NO_3^- profiles were in the range of 2.2 to 4.9 mmol C m^{-2} d^{-1}. We found that 60 - 75 % of the benthic carbon turnover was metabolized via oxic respiration, only 11 – 28 % through anoxic mineralization pathways, and the remainder by denitrification.

Evidence for re-oxidation processes at the redox boundary at sediment depths of about 2 cm was obtained from the shape of O_2 profiles and from an alkalinity balance established with flux rates of HCO_3^- calculated from pH and CO_3^{2-} profiles. It identified the carbonate-free sediment as a sink of alkalinity caused by buffering of H^+ generated by re-oxidation processes of reduced compounds such as Fe^{2+}, Mn^{2+} and NH_4^+ [1]. Dark CO_2 assimilation by chemoautotrophic bacteria was on the order of 0.03 - 0.1 mmol C m^{-2} d^{-1} and could be neglected in the organic carbon balance. Due to the long O_2 exposure of 25-2500 years only 3-14 % of the settling organic carbon estimated from sediment traps and water column data is finally buried in the sediments of Lake Baikal [2].

References

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Isotopic effects in reactive fluid-rock systems with fracture-dominated flow and matrix diffusion

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Isotopes are used broadly to characterize reactive fluid-rock systems. Most modeling assumes 1D-porous flow and mineral-fluid reaction rates fast enough to maintain "local equilibrium." In fractured rocks, isotopes in both fluid and solid exhibit different behavior than in simple porous flow. The departure from the porous flow model depends on the diffusivities of dissolved species in matrix pore fluid, their solubility, and the mineral-fluid reaction rates. Isotopes can be used to evaluate the importance of diffusion-limited reaction zones in fluid-rock systems.

A mathematical model is developed that describes the effects of matrix diffusion on the isotopic evolution of fluids and rocks in systems with fracture-dominated flow. The approach generalizes previous models for radiocarbon ages of groundwaters, and those that assume infinitely fast fluid-rock exchange rates. The equations describe parallel equidistant fractures separated by slabs of porous "matrix" rock containing stagnant pore fluid. The effect of matrix diffusion on the isotopes of a particular element depends on the ratio of the diffusive reaction length (Ld) to the fracture spacing (b). Ld is a function of the mineral-fluid reaction rates within the matrix, the solubility and aqueous diffusivity of the element, and the matrix porosity. For $Ld/b < 0.3$, the fracture fluid exchanges isotopes only with a narrow zone of matrix within Ld of the fracture, and fluid-rock exchange produces an isotopic effect on the fluid that is smaller by $2Ld/b$ than for porous flow. For $Ld/b > 1$, the parallel fracture model is no different from a single porosity (1D porous flow) model. One element (e.g. O) can be in one regime while a second (e.g. Sr) is in the other.

The model is applied to Sr and O isotopic data from MOR and continental hydrothermal systems, and groundwater in fractured basalt. Data from multiple isotope systems for one aquifer can provide estimates of fracture spacing and fluid-rock exchange rates. For MOR systems, fracture spacing is estimated at 1-4m. For groundwater systems, fracture flow results in underestimates of fluid-rock exchange rates for some elements.