

Quantitative interpretation of pH distributions in aquatic sediments: A reaction-transport modeling approach

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Despite its status of master variable, there have been relatively few attempts to quantitatively predict the distributions of pH in biogeochemical reactive transport systems. Here, we propose a theoretical approach for calculating the vertical porewater profiles of pH and the rates of proton production and consumption in aquatic sediments. In this approach, the stoichiometric coefficients of species that participate in acid-base equilibrium reactions are treated as unknown variables in the biogeochemical reaction network. The mixed kinetic-equilibrium reaction system results in a set of coupled differential and algebraic equations and is solved using a new numerical solver that can handle both steady state and transient simulations. The diagnostic capabilities of the model are illustrated for depositional conditions representative of those encountered on the continental shelf. The early diagenetic reaction network includes the major microbial degradation pathways of organic matter and associated secondary redox reactions, mineral precipitation and dissolution processes, and homogeneous acid-base reactions. The resulting pH profile in this baseline simulation exhibits a sharp decrease below the sediment-water interface, followed by an increase with depth and again a decrease. The features of the pH profile are explained in terms of the production and consumption of protons by the various biogeochemical processes. Secondary oxygenation reactions are the principal proton producers within the oxic zone, while reduction of iron and manganese oxyhydroxides are primarily responsible for the reversal in the pH gradient in the suboxic zone. Proton production in the zone of sulfate reduction outweighs alkalinity production, maintaining the undersaturation of the pore waters with respect to calcite. Integrated over the entire depth of early diagenesis, dissolution of CaCO_3 is the main sink for protons. Variations in the reaction rate order and rate constant for CaCO_3 dissolution do not fundamentally alter the shape of the pH profile. An entirely different shape is obtained, however, when the pore waters are assumed to remain in thermodynamic equilibrium with calcite at all depths. The intensity of pore water (bio)irrigation has a major impact on pore water pH and may increase the difference in pH between the irrigated zone and the underlying, non-irrigated sediment.

Oxygen diffusion and consumption in eroding black shales: A control on long-term atmospheric oxygen

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Oxygen diffusion into eroding black shales leads to buried fronts of oxidizing ancient organic matter (OM) and pyrite. The related diffusion-reaction problem with surface erosion is examined by means of a one-dimensional numerical model with comparisons made to a recently completed field study near Clay City, Kentucky (Wildman et al., 2004); both of which exhibit regions (fronts) where OM and pyrite increase rapidly from near zero to finite values characteristic of the deep unoxidized sediments. In the model, downward oxygen diffusion is followed by Henry law partitioning into water films adsorbed on the reduced particles, where aqueous phase oxidation of OM and pyrite can take place under kinetic control. Sensitivity studies were conducted to examine details of the front morphology under the influence of different particle sizes, mass fractions, tortuosity, erosion rate, atmospheric oxygen content, water saturation, etc. The results have relevance to global chemical cycling. We conclude that the long-term oxygen evolution in the atmosphere is controlled primarily by the erosion rate and the quantity of OM and pyrite being exhumed from depth via erosion, rather than depending upon the atmospheric oxygen content. Only for extremely rapid erosion rates would finite amounts of ancient OM be eroded (and rapidly reburied). The numerical problem is challenging due to the stiff equations that arise from the rapid pyrite kinetics, along with the fact that OM, pyrite and oxygen can completely disappear. Evolution toward a steady-state solution is possible only for non-zero erosion rates. Box models utterly fail to capture the dynamics relevant for oxygen flux calculations relevant to the evolution of atmospheric composition. We may also comment on other isotopic and trace element diffusion studies underway.

References

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