Quantitative Chemical Mass Transfer in Coastal Sediments During Early Diagenesis: Effects of Biological Transport, Mineralogy, and Fabric

Yoko Furukawa
Seafloor Sciences Branch
Naval Research Laboratory
Stennis Space Center, MS 39529
phone: (228) 688-5474 fax: (228) 688-5752 email: yoko.furukawa@nrlssc.navy.mil

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LONG-TERM GOAL

The long-term goal is to develop a better mechanistic and quantitative understanding of the couplings between biologically enhanced transport, biogeochemical dynamics, and sediment fabric in coastal marine sediments.

OBJECTIVES

The objectives for FY00 were (1) to quantify and numerically model the solute and particle transport processes in cohesive coastal sediments as functions of depth-dependent burrow distribution, ratio of active to abandoned burrows, macrofauna metabolism, and burrow flushing frequencies; (2) to use the numerical model for theoretical hind- and fore-casting of biogeochemical mass transfer in cohesive coastal sediments, and (3) to continue the use of nanoscale tools (i.e., energy-filtering transmission electron microscopy (EFTEM) and electron energy-loss spectroscopy(EELS)) to investigate the relationship between organic carbon (OC) reactivity and microfabric parameters. The short-term goals included (I) quantitative description of biologically-enhanced solute transport (i.e., bioirrigation) and particle transport (i.e., bioturbation) in the field and laboratory mesocosm sediments that explicitly considers depth-dependent burrow distribution, ratio of active to abandoned burrows, infauna metabolism, and burrow flushing frequencies; (II) model coding and parameterization strictly constrained by the actual field and laboratory mesocosm data; and (III) continued nanofabric investigations of the field and laboratory mesocosm samples.

APPROACH

My field and laboratory approach for the bioirrigation/bioturbation study was to analyze the spatial and temporal distribution of intrinsic solute tracers (NH_4, PO_4, SO_4, and TCO_2, using standard methods of spectrophotometry, ion chromatography, and potentiometric titration) in conjunction with the depth-dependent burrow distribution (by X-radiography), ratio of active to abandoned burrows (by X-radiography and animal counts), and burrow flushing frequencies (by visual observations of flushing events aided by the use of deliberate solute tracers). Benthic mesocosms were built and maintained, under the ONR-funded collaboration among Sam Bentley (LSU), Dawn Lavoie(NRL), and myself to simulate low-energy, heavily bioturbated fine-grained estuarine sediments. Sediments from the benthic mesocosms were characterized for all parameters listed above. Sediments from field test sites (St. Louis Bay and Horn Island, Mississippi, and Dry Tortugas, Florida) were characterized through the same collaboration for the parameters listed above except the burrow flushing frequencies. *Schizocardium* sp. was used in the mesocosm experiments as the bioirrigator of choice, as it was found to be abundant in one of our field sites (St. Louis Bay), adaptable to the laboratory environment, and a rigorous bioirrigator that flushes its U- or V-shaped burrows in one direction. The data were used to write and test a solute transport model in which depth-dependent burrow distribution, ratio of active to abandoned burrows, infauna metabolism, and burrow flushing frequencies were explicitly considered.

The two-dimensional reactive transport model, with the organic carbon advection component, is based on the bioirrigation model geometry first described by Aller (1980) and later numerically modeled by Boudreau and Marinelli (1994) using the diffusion-reaction (DR) equation:

$$\frac{\partial C_{x,r,t}}{\partial t} = \frac{\partial}{\partial x}\left(D_{sw} \frac{\partial C_{x,r,t}}{\partial x} \right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{sw} \frac{\partial C_{x,r,t}}{\partial r} \right) + R \qquad (1)$$

where x is depth, r is radial distance from center of burrow, and D_{sw} is the diffusion coefficient in seawater. Concentration of a given species (C) is determined by the vertical diffusion perpendicular to the water-sediment interface, radial diffusion perpendicular to the burrow wall, and integrated reaction rate (R). I modified the model geometry so that the depth-dependent distribution of burrows can be explicitly handled. Also, I included the advective transport to the model equation (i.e., ADR equation) so that the non-steady state flux of OC and solute species to the seabed and burrow walls may be explicitly handled:

$$\frac{\partial C_{x,r,t}}{\partial t} = \frac{\partial}{\partial x}\left(D_{sw} \frac{\partial C_{x,r,t}}{\partial x} \right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{sw} \frac{\partial C_{x,r,t}}{\partial r} \right) - v\frac{\partial C_{x,r,t}}{\partial x} + R \qquad (2)$$

where v is the advection velocity (i.e., sedimentation rate). Additionally, I implemented the production of metabolites (i.e., NH_4^+, TCO_2) by macrofauna (i.e., *Schizocardium* sp.) in order to handle the elevated metabolite concentrations within burrows compared to surrounding sediments where microbial metabolism is the only factor.

My technical approach for the nanoscale OC mapping was the same as it was in FY99---to image the distribution of carbon within clay aggregate samples from St. Louis Bay and benthic mesocosms using EFTEM. EFTEM has an advantage over the traditional staining techniques for the OC visualization because the investigators do not have to rely on the assumption that all sedimentary OC has recognizable morphological features. Thus, EFTEM allows unveiling OC that does not exhibit well-studied features such as polysaccharide webs and cell structures. Epoxy resin, a common embedding medium for the preparation of sedimentary samples for electron microscopy, is a carbon compound and would interfere with the mapping of intrinsic organic carbon. Consequently, I chose to use amorphous elemental sulfur as the embedding medium.

WORK COMPLETED

A set of experiments initiated during FY99, in which four tanks were each populated with 800 individuals/m^2 *Schizocardium* sp., was completed under collaboration with Sam Bentley (LSU). I analyzed variables necessary for properly constraining the pore water irrigation model, such as the depth distribution of pore water solute species. Burrows were characterized by Sam Bentley (LSU) and Dawn Lavoie (NRL). The data have been used to constrain the 2D ADR reactive transport model. The data has also been provided to Carla Koretsky (Western Michigan U.) and Philippe Van Cappellen (Utreht U.) recently, so that their stochastic irrigation model (Koretsky et al., 1999) and inverse model (Meile et al., 2000) will be applied.

One trip to St. Louis Bay test site and two trips to Horn Island test site were completed along with the analyses of the spatial distribution of solute species, burrow geometry and distributions, and animal populations. Sam Bentley (LSU) collaborated in all field trips and was in charge of radiochemical sedimentology (e.g., ^{210}Pb, ^{234}Th, ^{7}Be).

The 2D numerical model for advection, diffusion, and reaction has been upgraded since the FY99 report to accommodate depth-dependent burrow distribution, advection, and infauna metabolism. The model also explicitly utilizes information on ratio of active to abandoned burrows and burrow flushing frequencies. The model was applied to data from the benthic mesocosms as well as the field data from Dry Tortugas, Florida. The model is currently being applied to the data obtained in St. Louis Bay and Horn Island.

Spatial mapping of organic carbon in 10-50 nm scale using EFTEM has been completed for clay-OC aggregate samples from St. Louis Bay. The mapping technique has also been utilized to analyze matrix, fecal mounds, and burrow wall samples from the benthic mesocosms.

RESULTS

Irrigation model---The 2D ADR model was applied to the laboratory benthic mesocosms and carbonate sediments of Dry Tortugas, Florida. Model applications to the laboratory benthic mesocosm data (Figure 1) show that the model, which explicitly accounts for the depth-dependent distribution of burrows and macrofauna metabolism, is capable of hindcasting the observed depth profiles of NH_4^+. The model analysis indicates that the metabolite contribution by macrofauna is quantitatively significant. Without the implementation of macrofauna metabolism, the model would significantly underpredict the observed NH_4^+ buildup. Model applications to the Dry Tortugas carbonates (Figure 2) illustrate the steep geochemical gradients that exist within a few millimeters of water-sediment interface and burrow walls. These steep gradients, together with the biologically induced particle mixing, force sediment particles to experience rapid geochemical oscillation, which may result in increased rates of dissolution and precipitation reactions that occur syn-depositionally.

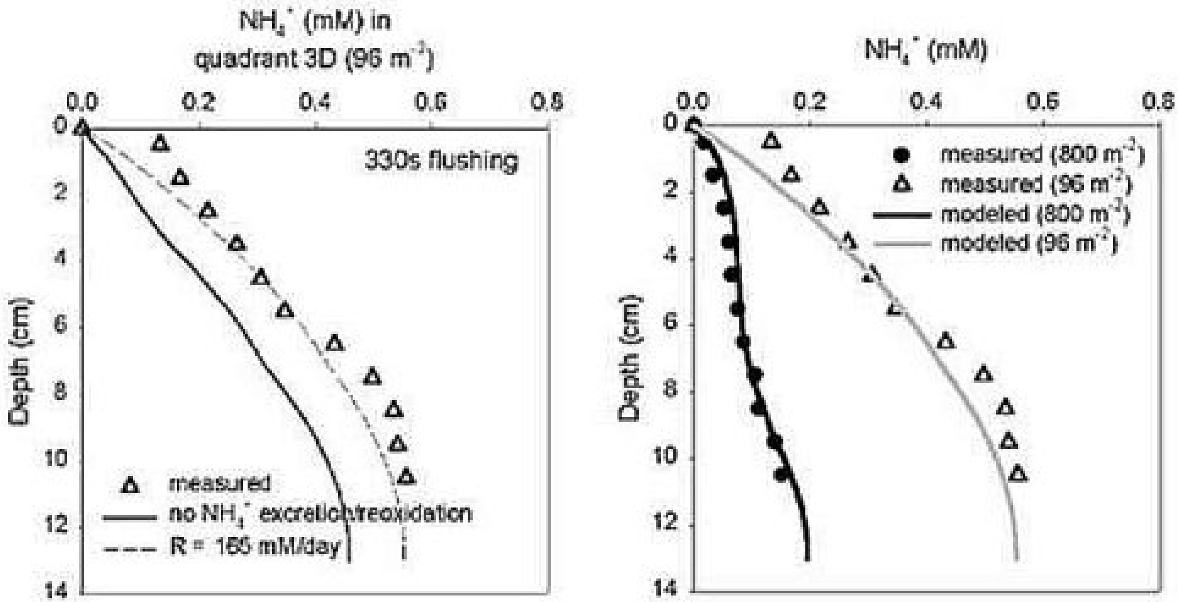

Figure 1. (A) Measured and modeled depth profiles of pore water NH_4^+ in a laboratory mesocosm with the animal density of 96 m^{-2}. When model was run with no implementaion of infaunal NH_4^+ excretion (solid line), the results underpredict the measured depth profile. On the other hand, when infaunal excretion of NH_4^+ at the rate of 165 mM/day is implemented between each flushing that occurs every 330 seconds, the model results agree well with the measured depth profile. (B) Measured and modeled depth profiles of pore water NH_4^+ in two laboratory mesocosms with different animal densities. The reasonable agreements between the measured and modeled profiles indicate that the forcings explicitly considered in the model (i.e., depth-dependent burrow distribution, metabolite excretion by macrofauna, and burrow flushing dynamics) are indeed significant.

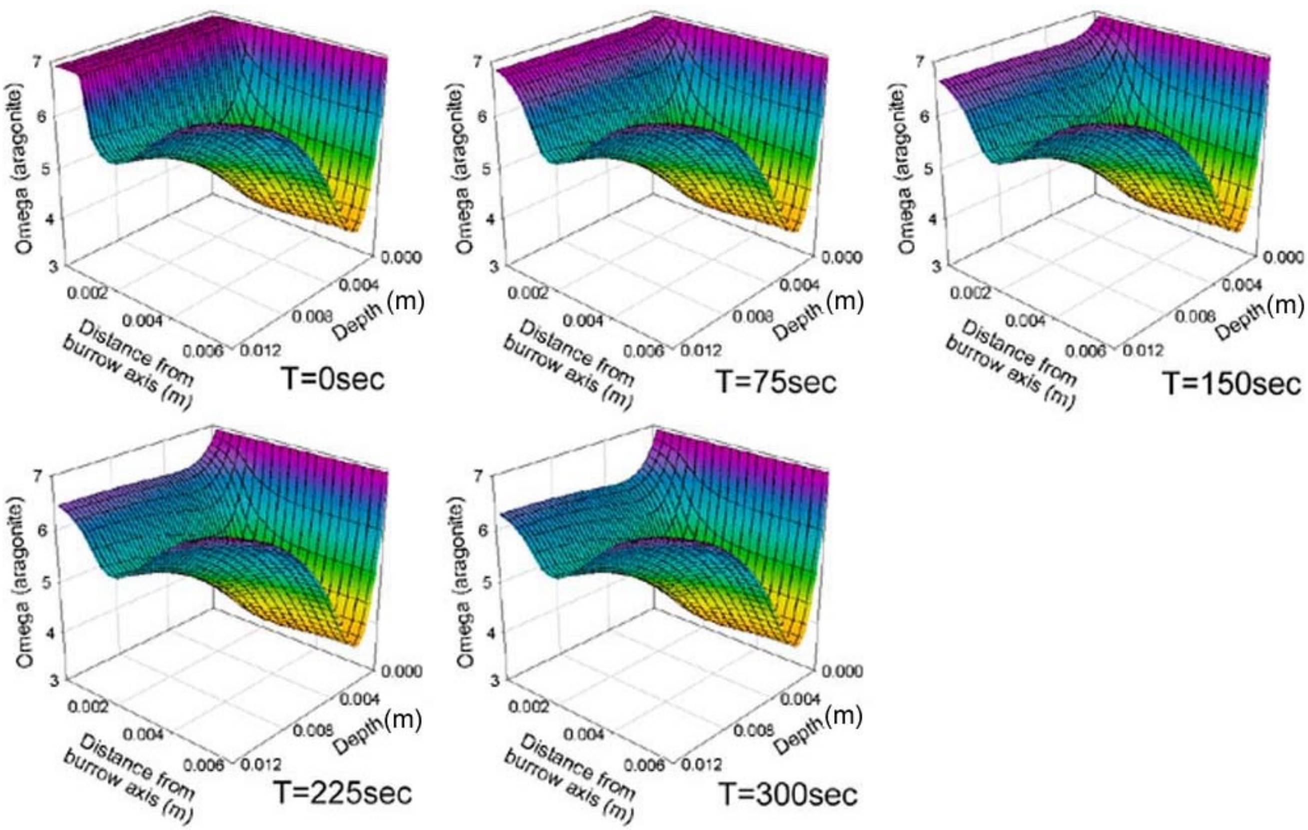

Figure 2. Modeled 2D spatial distributions of Ω (aragonite saturation state) in Dry Tortugas, Florida, during a complete cycle of burrow flushing. Flushing interval of 300 seconds was implemented. At the time of burrow flushing (T=0), the burrow water chemistry is reset to that of overlying water. The burrow water chemistry becomes closer to that of surrounding pore water while the burrow water is not flushed. Between a moment prior to next flushing (T=300) and at the time of the next flushing (T=0), pore water and sediment particles in the vicinity of burrow walls experience a rapid, dynamic chemical transition. The steep spatial geochemical gradients within a few millimeters of water-sediment interface and burrow walls are also evident. Although spatially confined to small zones, both static and dynamic chemical transitions occur where the biologically- and physically-mediated particle mixing is the most extensive. Consequently, the zones of steep gradients may play quantitatively significant roles in the chemical mass transfer during early diagenesis.

IMPACT/APPLICATIONS

The deterministic model for 2D reactive transport enables us to quantify the dynamic (i.e., non-steady state) nature of chemical mass transfer in aquatic sediments at very fine spatial and temporal resolutions. Such detailed and dynamic descriptions can be integrated to yield accurate bulk chemical information as well. This will allow quantitative descriptions of processes that have not been fully understood, such as the syndepositional simultaneous dissolution and precipitation of carbonates and rapid drop in pH immediately below the water-sediment interface. These quantitative descriptions will become a critical component for the base knowledge utilized for organic mine countermeasures because biogeochemial diagenesis (bioturbation, OC remineralization, authigenic mineral formation) is largely responsible for the observed physical, acoustic, and optical properties of nearshore sediments. Also, detailed, deterministic descriptions of sedimentary chemical mass transfer form a basis for assessing the consequences of environmental impacts that US Navy causes in harbors and coastal oceans.

RELATED PROJECTS

1 – Philippe Van Cappellen (U. Utrecht) and Carla Koretsky (Western Michigan U.), together with other collaborators (T. DiChristina, GA Tech; J. Haas, Western Mich. U.), are characterizing chemical mass transfer that occur in two field sites (Sapelo Island, GA, and Sheldt Estuary, The Netherlands). I plan to continue my participation by characterizing the burrow distribution and interpreting the spatial distribution of solute species using the 2D ADR model.

2 – Carla Koretsky (Western Michigan U.) and Philippe Van Cappellen (U. Utrecht) are developing a method for stochastic burrow generation. I plan to replace my current idealized burrow geometry with the stochastically generated sediment fabric in the future version of model.

3 – Tim Keen (NRL) and Sam Bentley (LSU) are studying the sedimentary history of Mississippi Sound using radionuclide methods and coupled numerical hydrodynamic-sediment transport model. I will utilize the results in conjunction with my geochemical data from Mississippi Sound for development and validation of non-steady state reactive transport model for early diagenesis.

4 – Tyrone Daulton (NRL) and I are working together to develop improved sample preparation and imaging techniques for TEM specifically for the imaging of fine-grained aquatic sediments. The resulting nanofabric images will be combined with bulk geochemical data to quantify the physico-chemical interactions between clay mineral surfaces, organic molecules, and microorganisms.

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