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

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LONG-TERM GOALS

Our long term goals are to provide a better quantitative and mechanistic understanding of chemical processes that occur in fine-grained coastal and continental margin marine sediments, especially with regard to how these processes affect biogeochemical fluxes and the transport and/or retention of environmentally sensitive natural and anthropogenically generated chemical compounds in coastal environments.

OBJECTIVES

The objective of this research is to make better predictions of chemical mass transfer in fine-grained siliciclastic coastal sediments, especially with regard to the impact of the biological effects, as well as on the influence of sediment mineralogy, fabric, and particle surface chemistry on the mechanisms of transport and the fluxes of biochemical species in coastal marine sediments.

APPROACH

Our approach combines the strengths of investigators from three institutions, Scripps Institution of Oceanography (SIO), The Naval Research Laboratory at the Stennis Space Center (NRL), and Georgia Technological University (GTU). This consortium is working together to integrate controlled laboratory experiments on the microbiological influences on sediment physical properties and chemical transport in model sediments (SIO) with field-based biogeochemical studies and sediment fabric/microfabric characterizations (NRL) and numerical reactive transport modeling (GTU). Overall objectives of the SIO program for the time period discussed were to explore the specificity between anaerobic microbial consortia and sediments composed of different clay minerals, the effect of microbes on a variety of toxic metal species in solution, test and calibrate an osmotic pumping system for *in situ* pore fluid sampling, and determine baseline behavior of the physical properties of model sediments with regard to their diffusive transport properties.

WORK COMPLETED

The SIO-directed part of the program involves uncoupling sediment-mineral-microorganism interactions using controlled laboratory experiments with model sediments and our specially designed reactors. A controlled laboratory program was initiated to examine whether there is a direct relationship between the mineralogy of fine-grained marine sediments and anaerobic microbial consortia that inhabit them. This was done for both sulfate- and iron-reducing anaerobic cultures enriched from the same initial natural consortia of microbes taken from fine-grained coastal sediments near SIO. Experiments were carried out in model sediments consisting of pure sterilized samples of the clay minerals that are most common in marine sediments: illite, smectite (var. montmorillonite), chlorite, and kaolinite. A sediment composed of pure quartz silt (20 µm) was also used. Experiments were also carried out that investigated the influence of dissolved species of Cr and Mn on natural microbial consortia. Reactors have been constructed and have been used to test osmotic pump sytems for *in situ* sampling of the chemistry of porewaters. Sediment conductivity studies were carried out and data were collected as a function of depth for different model sediments with different clay mienral compositions. Microbiological experiments were carried out with under the guidance of Dr. Bradley Tebo in his microbiological laboratories at SIO.

RESULTS

***Mineral-Microbe Specificity*:**

Initial experiments were carried out to examine the specificity for prokaryotes for different fine-grained sediments using five model sediments in anaerobic reactors because little is known about the specificity of prokaryotes for different fine-grained geological substrates (i.e., clay minerals and quartz) that dominate coastal marine environments. Minerals used in the experiments were five of the most common found in fine-grained sediments, illite, smectite (var. montmorillonite), chlorite, kaolinite, and quartz. A single natural bacterial consortium taken from fine-grained marine sediments near SIO and aliquots of its enrichment were used to innoculate each of the five different mono-mineralic model sediments which consisted of pure sterilized clay minerals or quartz silt. After 3 months incubation, DNA was isolated from the minerals and a 300 bp fragment of the small subunit 16S rRNA genes was amplified using Bacteria-specific primers. Denaturing gradient gel electrophoresis of the fragment followed by PCR and DNA sequencing of the major bands in the gel was used to determine the bacterial groups in the enrichment cultures. Several sequences from bacteria associated with kaolinite and chlorite were found that appear to be related to the genus Desulfomicrobium (95% similarity). Sequences associated with quartz and montmorillonite were most similar to Desulfovibrio (87-97% similarity). DNA extracts from the illite sample were of poor quality and could not be interpreted. Positive amplification of 16S rRNA gene fragments with Archaea-specific primers was obtained from all the iron-reducing enrichment cultures. These results suggest that different minerals may exert important controls on the composition of anaerobic microbial communities (Table 1).

Table 1. Mineral-microbe association for sulfate reducing enrichments with % similarity to known species in brackets.

Mineral Species	Bacteria (% Similarity to known genomes)
Kaolinite	Desulfomicrobium spp. (95%): escambium, hypogenium, baculatum Desulfobacterium macestii (95%)
Chlorite	Desulfomicrobium spp (90-93%): escambium, hypogenium, baculatum
Illite	no data, bad sequence
Montmorillonite	Desulfovibrio spp. (87%)
Quartz	Desulfovibrio acrylicus (97%)

Microbe-Metal (Cr, Mn) Interaction:

Two studies were carried out to examine the impact of the potentially toxic metals Cr and Mn on natural microbial cultures. The first study focused on chromium (Cr), a carcinogenic metal contaminant in many coastal waters whose origins are industrial processes and antifouling agents on the hulls of ships. Once in the marine environment, chromium occurs in two forms, hexavalent chromium (Cr(VI)) which is highly soluble and toxic and trivalent chromium (Cr(III)) which is relatively insoluble at neutral pHs and is formed under reducing conditions. Some bacteria are resistant to Cr(VI) in moderate concentrations, and some can reduce Cr(VI) to its non-toxic trivalent form. Results from our work show that metal- and sulfate-reducing bacteria grown in the absence and presence of Cr(VI) under aerobic and anaerobic conditions displayed differential protein profiles, indicating chromium-induced responses in protein synthesis. Further studies are now being carried out to identify and characterize the differential proteins, which could potentially elucidate the mechanisms of direct chromium reduction and/or chromium tolerance. These include the use of solid-state microelectrodes built to measure small gradients of iron, manganese, oxygen and sulfide near the sediment surface. In the coming year, environmental samples will be compared to laboratory experiments to determine which substances exert the most significant influence on chromium mobility and the role of bacteria will be examined by comparing the ability of sterilized vs. non-sterilized sediments to reduce chromium.

The second set of experiments were carried on the effect of redox gradients on bacterial Mn (II) oxidation using a natural bacterial isolate from an aquatic environment rich in Mn, Zn, Ni, Co and Cu. Results showed that during the run, discrete Mn oxide bands were precipitated by the microbes and mm-scale micro-electrode voltammetry indicated that O_2 penetrated only the upper portion of the cultures within the five month experimental run. A simple linear diffusion model based on this data placed the maximum Mn (II) redox potential at approximately the same depth as the observed oxide bands. The resulting model predicted bands higher in the gradient than those exposed to atmospheric (~21%) O_2 concentrations. No concomitant oxidation occurred in sterile controls. Genetic information on the consortium showed bacterial 16S rRNA gene diversity within the oxide bands that was estimated using RFLP and sequencing analyses showed that *b* and *g Proteobacteria* dominated the population, representing 58% and 33%, respectively, of unique RFLPs sequenced to date. These data indicate that Mn (II) oxidation of our isolate is associated with a diverse group of *Proteobacteria*, some of which appear to oxidize Mn (II) under specific redox potentials. Further study of the effects of redox gradients and bacterial Mn (II) oxidation is in progress.

***Osmotic Pump Testing and Calibration*:**

Osmotic samplers using salt gradients and membranes, calibrated for medical purposes, have been successfully tested and calibrated for making high resolution time-series sampling of marine sediment pore waters. Pore waters are drawn through the osmotic process up into long capillary tubes, initially filled with distilled water (see Figure 1 below). Pore waters displace the distilled water. To sample, capillary tubes are crimped into lengths that provide the resolution and amount of solution required for the objectives of a particular study.

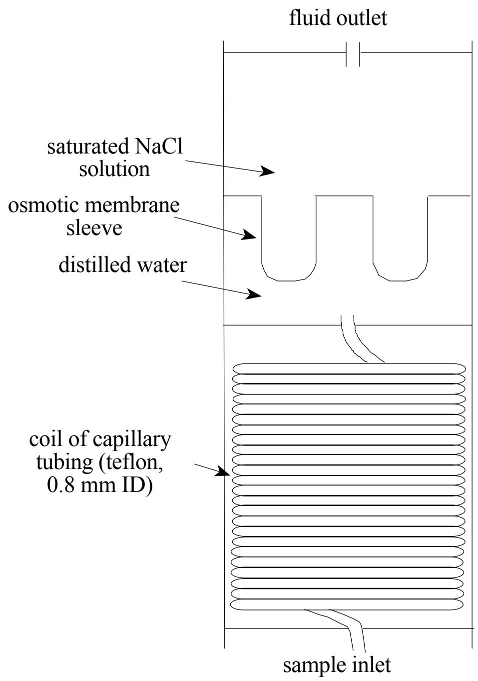

Figure 1. Schematic diagram of osmotic pump for pore fluid sampling.

Sediment Conductivity Experiments:

Investigations of sediment conductivity show distinct differences in behavior between pure sediments comprised of kaolinite, chlorite, quartz, and montmorillonite, with montmorillonite showing the largest effect. Calculations are being carried out to determine the impact of these results on calculated sediment formation factors and the impact the differences have on diffusional geochemical fluxes.

IMPACT/APPLICATION

Results from the mineralogical controls on sediment physical properties and on the development of anaerobic microbial communities in fine-grained coastal marine sediments further our understanding of the importance of minerals in biological processes, how prokaryotes physically interact with the clay mineral components of fine-grained sediments, and how they alter sediment physical properties. Results can also be used to better understand and model the cycling of nutrients and other biogeochemical species between sediments and the ocean.

TRANSITIONS

Model sediments developed in this project are being used by microbiologist Dr. Bradley Tebo and his research group at the Scripps Institution of Oceanography to determine the specificity of bacterial consortia for sediments comprised of different clay mineral suites.

PUBLICATIONS

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