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

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LONG-TERM GOALS

Program goals were to train graduate and undergraduate students in sedimentological, chemical, biological, and physical property research and data analysis in coastal marine systems. This was achieved by including students as active participants in research focusing on providing a better quantitative and mechanistic understandings of chemical processes in fine-grained coastal and continental margin sediments. The focus was on how these processes effect biogeochemical fluxes and the transport and/or retention of environmentally sensitive natural and anthropogenically generated chemical compounds in coastal environments.

OBJECTIVES

Objectives of this effort were to provide hands-on research training in laboratory and field aspects of marine sedimentological research, as well as in data analysis, experimental design, and hypothesis testing. The vehicle used was a concurrently funded laboratory research program examining fundamental questions in fine-grained sediment geochemistry. Questions addressed were: (1) what are the controlling sediment and physical mineralogical factors in adaption of different microbial communities to their host sediments; (2) what is the specific impact on sediment chemical transport on the occultation of sediment pores by organic matter, both living and dead; (3) does the specificity of distinctly different microbiological consortia seen in the laboratory carry out into the natural environment; and (4) is there an observable effect of the different consortia on environmentally hazardous compounds in the natural system.

APPROACH

As part of a three institution, coalition working to gain a quantitative and mechanistic understanding of chemical mass transfer in coastal marine sediments, efforts at the Scripps Institution of Oceanography

(SIO) focused on the impact of mineralogy on sediment physical, biological, and chemical properties. Collaborators at the Naval Research Laboratory at the Stennis Space Center (Drs. Y. Furukawa, D. Lavoie, and associates) were focused on field and microfabric aspects of this work, and collaborators at the Georgia Technological University (Drs. Philippe van Cappellan, C. Koretsky, and associates) were responsible for combining these results into the computational part of the program.

At Scripps work was carried out, over the course of the funding period by three graduate students (Karen Murray, Kimberly Cobb, and Christian Solem) and six undergraduates (Holger Michaelis, Margret Imhof, Kim Brower, Leah Powers, Vahid Fozi, and Garth Englehorn), all of whom are U.S. nationals. Their work involved assisting in the characterization of the model sediment materials and in the design, construction, and running of the reactors, as well as in data collection and data analysis. Students also played a major role in our metal oxidation and permeability studies and were trained in the use of resistivity probes and micro-electrodes. For the microbiological studies, anaerobic conditions were imposed in either Fe-reducing or S-reducing environments. Gel electrophoresis and other standard molecular biological techniques were used to determine microbial community structure. Microbiological work at SIO was carried out in collaboration with Dr. B. Tebo, his students, and his laboratory.

WORK COMPLETED

Chemical and physical characterization of the pure minerals used in the experimental program were made. Resistivity measurements and calibrations were done for model sediments of different mineralogy, focusing primarily on pure clay mineral end members and clay-rich sediments. Theoretical models and algorithms were generated to permit assessment of the impact of both hydrated clay minerals and organic matter, living and dead, on sediment porosity and geochemical fluxes; and results were made available to our collaborators for incorporation into computer models of reactive mass transfer in marine sediments.

Laboratory reactors for continuous monitoring of mesocosm studies were built and an innovative new osmotic pump for time series analysis of pore water chemical changes was developed and used successfully in both laboratory and field settings. Field and laboratory controls on the biogeochemical cycling of toxic chromium in harbor sediments in San Diego Bay, California were examined in terms of elucidating the relative importance of biotic versus abiotic factors in chromium (IV) reduction. Also carried out were an extensive series of experiments to examine the impact of mineralogy on anaerobic microbial communities and determine possible specificity of microbes for different mineralogical entities, in particular different clay minerals. Experiments for both Fe- and S-reducing communities were successfully carried out and analyzed by molecular biological techniques (e.g., gel electrophoresis, PCR, and DNA sequencing) to identify differences between the microbial communities.

More extensive determination of the microbial communities of the anaerobic experiments are still yet to be made, but we expect these to be completed within the next fiscal year. Also to be completed are more detailed mesocosm measurements of biological mediation of toxic chromium in marine sediments. These are presently being carried out under funding of the EPA. Also to be completed are three manuscripts presently under preparation on the impact of organic matter occluding sediment pores on geochemical fluxes, a microfabric model for organic matter preservation, and the results of our microbiological experiments on mineral-microbe interaction and specificity.

RESULTS

The primary conclusions and results from the study during the last fiscal year were that organic matter in clay-rich sediments occludes a significant percentage of the total intergranular pore spaces, with measurable impacts on geochemical fluxes into and out of the seafloor. Depending on the amount of organic matter present and the total classically determined sediment porosity, this material can occlude up to 20% of the available pore spaces.

A second discovery was that minerals with similar structures, but with different chemical compositions physical interactions with water and its dissolved constituents, promote the growth of different bacterial species in anaerobic sedimentary environments (Tables 1 and 2). These conclusions resulted from reactor studies in which a single original natural consortium of bacteria were taken from offshore of SIO and then enriched under sulfate- and iron-reducing conditions. Aliquots of the enriched cultures were then put into reactors with model sediments composed of a single mineral type. After incubation for three or more months, it was found that different clay minerals enhanced the development of different microbial communities. This result has interesting and potentially promising applications for stabilizing and enhancing microbial communities in aquatic environments in the contest of bioremediation applications.

Table 1. Major differences in microbial communities that originate from the same initial microbial innoculant for each model sediment. Results are presented for the sulfate-reducing microbial enrichments.

Mineral	Mineral Composition and Structural Formulae	Microbial Biodiversity Differences (% DNA Similarity)
Quartz	SiO_2	desulfovibrio acrlicus (97%)
Kaolinite	$Al_2Si_2O_5(OH)_4$	desulfomicrobium spp. (95%) escambium hypogeium baculatum desulfobacterium macestii (95%)
Chlorite	$(Fe,Mg)_3Fe_3(AlSi_3)O_{10}(OH)_8$	desulfomicrobium spp. (95%) escambium hypogeium baculatum
Illite	$K_{0.8}Al_{1.9}(Al_{0.5}Si_{3.5})O_{10}(OH)_2$	no interpretable data
Smectite	$K_{0.3}Al_{1.9}(Si_4)O_{10}(OH)_2*4.5H_2O$	desulfovibrio spp. (87%)

Preliminary results of the toxic chromium mesocosm study show that there are distinct differences in the redox conditions of marine sediments with high levels of chromium pollution and that bacterial mediation of these reactions has a significant impact on the rate of chromium transformation to its less toxic oxidation state.

Table 2. Major differences in microbial communities that originate from the same initial microbial innoculant for each model sediment. Results are presented for the iron-reducing microbial enrichments.

Mineral	Mineral Composition and Structural Formulae	Microbial Biodiversity Differences (% DNA Similarity)
Quartz	SiO_2	clostridium thermoplarium (93%) shewanella alga (99%)
Kaolinite	$Al_2Si_2O_5(OH)_4$	shewanella alga (98%)
Chlorite	$(Fe,Mg)_3Fe_3(AlSi_3)O_{10}(OH)_8$	vibrio spp. (95%) clostridium spp. (91-96%) thermopalarium dysprosium shewanella alga (97-98%)
Illite	$K_{0.8}Al_{1.9}(Al_{0.5}Si_{3.5})O_{10}(OH)_2$	acinetobacter spp. (95%) shewanella putrifaciens (94%)
Smectite	$K_{0.3}Al_{1.9}(Si_4)O_{10}(OH)_2*4.5H_2O$	shewanella alga (99%)

IMPACT/APPLICATION

Incorporation of a method to repartition water back into hydrated sediment phases such as smectite and organic matter in natural marine sediments, permits more accurate calculations of true sediment porosity and geochemical fluxes to be made for seafloor sediments. But perhaps our most important finding is that of microbial specificity for sediments composed of different minerals. This discovery allows us to now explore the possibility of designing long-term stable microbial consortia that can be put onto the seafloor and remain in place for remdediation of underwater toxic contaminants. Using mineralogical substrates that enhance the competitiveness of resident microbiological communities that have been genetically engineered to breakdown a specific compound, designer microbial consortia now have a chance to remain relatively immobile at the underwater location at which remediation must occur. Because most of the clay minerals used in our studies are abundant and relatively inexpensive to obtain, this creates the possibility of highly cost-effective long-term microbial remediation of underwater contaminant sites, something that up to now has eluded us.

TRANSITIONS

Focusing on biogeochemical fluxes in fine-grained sediments, the scope and impact of this work and its training of students expanded from the original project's contributions into the fields of: (1) molecular biology and microbial remediation of toxic metals and organic compounds, (2) continental margin gas hydrate sediment chemical and physical properties and (3) climate change. Collateral collaborations primarily included the microbiological laboratory of Dr. B. Tebo, Dr. H. Jannasch of the engineering staff at MBARI (Monterey Bay Aquarium Research Institute), and Y. Weinstein an Israeli hydrogeologist on a two year visit to SIO. The funding permitted investigation of conditions of bioremediation of toxic chromium in sediments and the development and testing of a new osmotically driven sediment fluid sampler which has been deployed to monitor and record small-scale sediment hydrology and geochemical changes for periods that can extend in length for more that a year.

RELATED PROJECTS

Funding for this ASSERT grant was tied closely to the goals of an ONR-funded proposal of the same name and with the same P.I.s that consisted of a collaboration between the Scripps Institution of Oceanography, the Naval Research Laboratory at the Stennis Space Center, and the Georgia Technological University for the purpose of quantifying chemical mass transfer in fine-grained coastal marine sediments.

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