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Organic Coatings on Sedimentary Mineral Grains

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Organic Coatings on Sedimentary Mineral Grains

Project Participants

Senior Personnel

Name: Mayer, Lawrence
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Graduate Student

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities:

This project started as an investigation of organic matter-mineral interactions as protection mechanisms against biological attack. Over the course of the project, I developed and applied a method to use high-resolution BET analysis to the interpretation of organic matter coverage of mineral surfaces. Sediments and soils from sites from around the world were analyzed. This work fulfilled the intentions of the original grant.

The emerging emphasis on the role of clays in organic matter protection stimulated method development to isolate clay-organic matter associations. We built on previous work in this area by developing high-density sodium polytungstate solutions that provided rather clean separates. We characterized these associations using a variety of organic matter and mineral characterization techniques, including the BET method described above.

Upon being given a Creativity Extension to this grant, I inaugurated research in several areas related to the lability of organic matter. I used the freedom granted by this Extension to test some new and risky ideas.

Following up on the BET method (above), I developed a method to ascertain the filling of small mesopores by organic matter, a configuration that was previously hypothesized to prevent enzyme access to the organic matter. During the course of this development, I also developed a method to determine the mass density of organic matter in sediments and soils, using high-resolution gas pycnometry. These methods were applied to a series of soils and sediments from around the world, focusing on samples that represent the major burial fluxes and storage sites of organic matter.

A second area of research was to follow up on some literature that used photochemical degradation of soil organic matter with high-intensity

UV radiation as a probe of organic matter-mineral interactions. In my case I used a solar simulator, as a test of photochemical degradation of organoclay aggregates in earth surface environments. I did development work and preliminary experiments, which were packaged to become a successful subsequent proposal to the NSF Carbon Cycle Program.

A third area was the formation of refractory organic matter in the water column via partial oxidation reactions of biopolymers. My approach was inspired by recent work in the biomedical literature on oxidation-induced pathologies. The first foray was into the oxidation of tryptophan moieties in proteins. This reaction has been hypothesized as a pathway for protein degradation and formation of colored, refractory compounds in systems such as eye cataracts. I developed the analytical methodologies for reactants and likely products, and applied them to experiments in which starting materials such as algal cells were allowed to decay.

Within this general theme, I explored the role of lipid oxidation and subsequent conjugation to amines (e.g. proteins), following up on earlier oceanographic literature by G. Harvey and R. Kieber, supplemented by a recent advances in biomedical areas. Experiments with various simple reactant systems (e.g., aldehydes and amino acids) were followed up by decay experiments with more complicated systems (e.g., rotting algae). Reactive intermediates (e.g., hydroperoxides, aldehydes) and products (e.g., FDOM, reduced hydrolyzability of proteins) were tested.

Following up on preliminary results from a parallel project, I supported one of my students (Anders Giessing) to examine the potential role of invertebrate digestive peroxidase enzymes in causing conjugation of reactive phenolic groups. This type of reaction has been found to be important in soil systems (via inorganic oxide catalysis). Both natural (tyrosine) and xenobiotic (1-hydropyrenol) compounds were tested.

Findings:

Successful testing of a method for determination of organic coatings on mineral grains allowed a test of the meaning of ômonolayer-equivalentö loadings of organic matter that dominate many marine sediments. The actual coverages found were far less than complete monolayers, instead implying that organic matter in sediments is present as discrete ôblebsö that typically cover 1-20% of mineral surfaces. Full coverage of mineral grains can be found only in sediments that exhibit much higher organic matter loadings. This work was subsequently extended to soils, for which similar results were found. Use of similar analytical approaches for soils and sediments helps to validate ways in which organoclay aggregates are similar vs. different for terrestrial vs. aquatic environments, enhancing synergies between marine and soil science communities.

Upon isolation of clay-organic matter associations, we found that major portions of organic matter in Gulf of Maine sediments were in this form, residing in the 2.2-2.4 g/mL density range. The inorganic fraction was composed primarily of thin clay particles, with average c-axis thicknesses of 25-30nm. Intergranular pore size distributions were similar to those found for bulk sediments. The mesopore protection hypothesis was therefore revised to focus on inter- rather than intragranular pores. This work was then generalized by applying these methods to a series of sediments from the shelf and slope off of Cape Hatteras.

Similar work on soils showed similarities with respect to clay control of organic matter associations and dominance of naked mineral grains rather than extensive coatings by organic matter. This work also illuminated differences, such as more prominent roles of soil pH and of metal sesquioxides in soil organic matter associations. Comparison with the liberation of surface area upon organic matter removal was instructive and helped to lead to the following projectÆs results.

Subsequent development of a means to test if the organic matter blebs reside inside or outside of small mesopores allowed a test of the mesopore exclusion hypothesis û viz, that organic matter held in these pores is physically protected from enzyme attack by size exclusion of the enzymes. We found that only small fractions of total organic matter in most sediments and soils of moderate organic matter loading are indeed held inside of smaller mesopores that are capable of excluding enzymes. Thus, some organic matter should be protected in this manner, but the hypothesis cannot explain protection of the majority of the total organic matter. Our determinations of the density of organic matter in sediments and soils represent the first such determinations made without chemical extraction and processing of the organic matter.

Exposure of Mississippi River suspended sediments to sunlight in a solar simulator demonstrated that the earth-surface, photolysis reactions, commonly observed to break high molecular weight dissolved organic matter into lower molecular weight forms, are also capable of causing significant desorption of organic matter from particulate into dissolved phases. Further, the extent of this reaction is similar to the organic carbon loss found in the transition from the river to the shelf deposit. This mechanism thus becomes a viable alternative explanation for the major carbon losses observed in large deltaic systems. While the initial discovery occurred under the Creativity Extension funding, detailed tests of the chemical nature and field viability of this reaction are continuing under the new NSF grant.

The exploration of tryptophan oxidation failed to find any of its oxidation intermediates in decay experiments. This negative result led to termination of this series of experiments. The subsequent exploration of lipid oxidation reactions has shown more success, though not enough to make a complete and convincing case. We find evidence for the appearance of appropriate reactive intermediates, such as lipid hydroperoxides, just prior to the onset of fluorescent compounds that are indicative of humified organic matter (FDOM). Further, we can enhance the production of this FDOM by adding lipoxygenase enzymes (which accelerate lipid oxidation) and inhibit it by adding lipoidal antioxidants (e.g., BHT). Last, using simple compound experiments that link lipid aldehydes with amino acids, we can produce compounds with similar fluorescence spectra as the FDOM produced during algal rot experiments. ADD IN EHAA EXPS. Our work may provide a mechanistic basis for the recent discovery from E. DruffelÆs lab that refractory DOM has isotopic signatures suggestive of lipid backbones.

In a serendipitous discovery, we found and followed up on the discovery that deposit-feeding invertebrates in sediments contain peroxidase enzyme activity in their guts. This discovery led to the possibility that phenolic compounds may be covalently polymerized by gut passage. We found that we could create humic-type compounds using gut fluid incubations with hydroxylated aromatic compounds. Tyrosine, a common constituent of proteins, was found to form dityrosine, which is often used as a marker in various free-radical-based disease pathologies. This work both demonstrates a mechanism for refractory organic matter genesis in sediments and leads to a possible biomarker for its occurrence in the environment. In a different context, this work extends the series of papers from our lab showing the diagenetic impact of gut passage on various sedimentary chemicals û inorganic and organic û providing a window on an oft-ignored pathway for chemical change in marine sediments.

Training and Development:

This work provided projects for several undergraduates via summer stipends paid by the grant or the REU program. Two graduate students û Anders Giessing and Rota Wagai û have received research support from this grant.

Outreach Activities:

The high-resolution BET method developed in the grant has application to industrial issues that require determination of organic coatings on inorganic substrates û e.g. fouling of cracking catalysts, coating of paper, and treatment of wall-board material. I have contacted various persons interested in these issues and shared my work with them. I also wrote a research article for a company-originated trade publication to expand awareness of this method.

The rest of the research has gotten exposure via the usual round of school visits and so forth.

Journal Publications

Mayer, L.M., "Extent of coverage of mineral surfaces by organic matter in marine sediments", Geochimica et Cosmochimica Acta, p. 207, vol. 63, (1999). Published

Bock, M. and L. Mayer, "Mesodensity organo-clay associations in a nearshore sediment", Marine Geology, p. 65, vol. 163, (2000). Published

Mayer, L.M. and B. Xing, "Organic carbon-surface area-clay relationships in acid soils", Soil Science Society of America Journal, p. 250, vol. 65, (2001). Published

Mayer, L., L. Benninger, M. Bock, D. DeMaster, Q. Roberts and C. Martens, "Mineral associations and nutritional quality of organic matter in shelf and upper slope sediments off Cape Hatteras, USA: A case of unusually high loadings", Deep-Sea Research, p. 4587, vol. 49, (2002). Published

Giessing, A.M.B. and L.M. Mayer, "Oxidative coupling during gut passage in marine deposit-feeding invertebrates", Limnology and Oceanography, p. , vol. , ( ). Submitted

Mayer L., Schick L., Hardy K., Wagai R. and McCarthy J., "Organic matter content of small mesopores in sediments and soils", Geochimica et Cosmochimica Acta, p. , vol. , ( ). Submitted

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

This research has refined the mineral-based, organic matter protection hypothesis that underlay the original proposal, rejecting incorrect forms of the hypothesis and bringing it along to new testable forms. Along the way, it has provided new insight into levels and mechanisms of organic matter protection in a variety of environments, including both the oceans and terrestrial soils. New mechanisms of organic matter protection and destruction have been elucidated, including some that do not necessarily involve minerals (e.g. photochemistry and animal ingestion).

Contributions to Other Disciplines:

This work has spilled over into the soil science area, involving the PI in several soil-based projects and leading to a keynote lecture invitation at a soil organic matter conference next year.

Contributions to Human Resource Development:

Several students have received training due in part to the activities of this grant.

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

As noted, the high-resolution BET method is applicable to several measurements needed by industry. I do not know if the method has actually been used with commercial outcome.

Categories for which nothing is reported:

Organizational Partners

Any Book

Any Web/Internet Site

Any Product

Contributions: To Any Resources for Research and Education