

Using electrochemical methods to study redox processes and harvest energy from marine sediments

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Experiments designed to generate electrical power by the principles of a fuel cell are revealing how oxidation and reduction processes in marine sediments depend on mass transport, solution, solid phase, biological and external variables. By positioning graphite electrodes on either side of an oxic-anoxic interface, we are able to study specific half cell reactions and microorganisms responsible for extracellular electron shuttling between available electron donors and electron acceptors.

To date we have conducted field fuel cell experiments in estuarine, shelf, slope and ocean seep environments. Recent laboratory studies have focused on the role of reduced products of anaerobic respiration as electron donors. Our findings include these insights:

1. Dissolved and solid phase sulfides serve as the most immediate and quantitatively important electron donors in typical anoxic marine sediments.

2. Marine sediments enriched artificially with dissolved sulfide yield the highest sustained power output, followed by the same sediments supplied with methane, acetate, and nitrogen, respectively.

3. If a stationary anode is in continuous operation, mass transport of reductants to the electrode surface will severely limit oxidation reactions on times scales of months, in most seafloor environments including seeps.

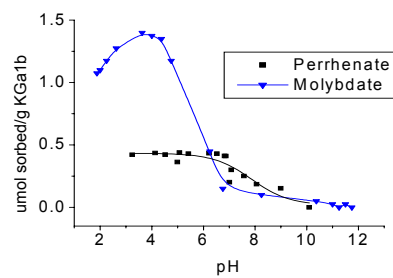
4. Active anode surfaces become coated with biofilms; however the microbial community composition and diversity of these biofilms has been shown to vary along an anode that crosses redox zones. This implies that many groups of microorganisms are capable of extracellular electron shuttling, and that the biofilms represent enrichments influenced by anode reactions, anode potential and the surrounding sediment.

The mechanism of Re fixation in reducing sediments

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Rhenium enrichment in sedimentary rocks is considered a paleoredox indicator, but chemical or biological mechanisms causing enrichment are uncertain. Consequently, what Re enrichment implies about paleoenvironments is unclear. The stable form of Re in oxic water is perrhenate (ReO_4^-), which in many respects behaves like MoO_4^{2-} in the ocean. The following figure relates ReO_4^- adsorption on kaolinite to that of MoO_4^{2-} (the latter determined by Goldberg et al. 1996; both at 0.3 mM in solution). Consistent with both anions' conservative behavior in the ocean, they are only weakly sorbed to



this common clay mineral near pH 8. If ReO_4^- is scavenged abiotically in reducing marine environments, either the sorbing agent has properties very different from kaolinite or preliminary "activation" of ReO_4^- occurs through reduction or ligand substitution. Thermodynamic and geochemical arguments show that Mn^{2+} , Fe^{2+} and NO_2^- are unlikely reductants for ReO_4^- . Experimentally, neither the H-atom donor, BH_4^- , nor H_2S are reactive on the time scale of hours, as judged by negligible promotion of Re scavenging by kaolinite. Even prior formation of thioperrhenates fails to promote scavenging by kaolinite. These results contrast with those for MoO_4^{2-} , which in the presence of H_2S is readily converted to thiomolybdate and scavenged by FeS (from trace Fe(III) in the kaolinite). The results of this study show that the marine geochemistry of MoO_4^{2-} is a poor model for predicting Re behavior. Instead, TcO_4^- , which is known to be microbially scavenged from solution, is a more promising model.

Reference

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Ferric Fe-isotopes in the early marine diagenetic cycle

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Early marine diagenesis under an oxic water column comprises a recurrent cycle of Fe-reduction / mobilization at depth and Fe-oxidation / precipitation in the surface layer. In reducing waters much of the ferrous Fe may escape from the sediments. Previous laboratory experiments have demonstrated that a fractionation of Fe isotopes occurs in many of the microbial and inorganic reduction and oxidation processes involved.

We have developed a leaching technique for Fe-oxyhydroxides based on a solution of KCl in N_2H_5OH that does not fractionate Fe-isotopes and from which Fe can be conveniently purified for mass spectrometric analysis. We present Fe-isotopes of natural ferric Fe leached from two marine surface cores from different redox environments in the Arabian Sea. One core is laminated and from the sediments inside the suboxic oxygen minimum zone (OMZ), the other is from the oxic waters below the OMZ. Both cores show light ferric Fe $\delta^{56}Fe$ (IRMM-14) values throughout. The laminated core shows a rapid decrease in the concentration of leachable Fe accompanied by $\delta^{56}Fe$ values increasing from -0.90 to -0.30 . The oxic core has a 4 - 5 cm brown oxic layer on top which shows little change in ferric Fe-concentration and $\delta^{56}Fe$ (-1.65 to -1.90). In the green sediments below the oxic layer ferric Fe-concentrations drop off and the $\delta^{56}Fe$ increases to -0.60 .

In both cores the increase in ferric Fe $\delta^{56}Fe$ within the section of Fe-reduction is only initially consistent with the fractionation expected during microbial dissimilatory Fe-reduction, suggesting that other factors, possibly Fe-reduction by H_2S , become important at greater depth. The bulk of the sediments in both cores is continental detritus ($\delta^{56}Fe \sim 0$) but the Fe-oxyhydroxides at the sediment surface before diagenetic modification are considerably lighter. This suggests that the reactive Fe has already been isotopically fractionated before deposition, for example during transport through the estuary, across the shelf, or down the continental margin. The overall lighter surface $\delta^{56}Fe$ values in the oxic core can best be explained by the early marine diagenetic Fe-cycle itself, which pumps isotopically light Fe from the zone of Fe-reduction into the oxic surface layer.

Molybdenum and molybdenum isotope diagenesis in continental margin settings: Geochemical balance and paleoproxy implications

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We measured Mo concentrations in marine pore fluids and sedimentary solid-phases, and solid-phase isotope values to ascertain Mo behavior during early diagenesis in reducing continental margin environments. We observe a non-linear relationship between oxygen penetration depth and Mo accumulation rate at sites where dissolved oxygen bathes the sediments. Coupled with this observation we observe linear relationships between (1) the accumulation rate of Mo and the organic carbon rain rate and (2) the isotope composition of Mo and the organic carbon rain rate. These combined relationships indicate that as oxygen penetration depth shallows to some critical depth, the reactions that govern authigenic Mo accumulation become sensitive to the rate of organic carbon delivery to the seabed and are independent of bottom water oxygen content. Our work suggests that continental margins are a net sink for Mo. Although the magnitude of this sink ($\sim 0.8 \pm 0.4 \times 10^8 \text{ mol y}^{-1}$) remains speculative, it may represent more than half of the removal term. Furthermore, a sink of this magnitude could alter current views regarding the processes controlling the distribution and availability of Mo through time.

Defining an uniquely euxinic molybdenum signal

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The redox chemistry of molybdenum and the implications of its enrichment in black shales is generally understood and often employed in the geochemical analysis of ancient marine environments. The conservative nature of the common oxidized species (MoO_4^{2-}) in sea water and its conversion to highly particle-reactive thiomolybdate ions (MoS_4^{2-}) where $\Sigma \text{H}_2\text{S}$ exceeds $\sim 10 \mu\text{M}$ suggests that its enrichment in black shales is indicative of the presence of reduced sulfur. Enrichments in black shales typically fall within a wide range of 5 to 400 ppm relative to an average crustal value of 2 ppm. This wide range of Mo concentrations has thus far prohibited the use of Mo enrichments as an unambiguous indicator of an anoxic/sulfidic (euxinic) water column.

On closer inspection we can demonstrate a distinct bimodality in the enrichment of Mo in modern sulfidic sediments. Mo concentrations in sediments where the sulfide interface remains below the seafloor do not exceed 16 ppm whereas those in euxinic environments are represented by a range of values of 20 to 200 ppm. This relationship suggests the presence of a barrier to the diffusion of Mo that disappears where dissolved sulfide reaches the sediment/water interface. We propose that this inhibition is associated with the presence of Mn-oxides in the sediment surface layer. The affinity of MoO_4^{2-} for Mn-oxides results in a subsurface maximum in dissolved Mo when these Mn-oxides are buried and dissolved, thus masking the Mo gradient between sulfidic sediments below and the water column above and prohibiting direct diffusion of Mo from seafloor into the sulfidic pore waters. As the sulfide interface reaches the sea floor, and euxinia sets in, this Mn cap disappears and the enrichment of Mo is then controlled by other factors such as Mo limitation in the water column, seasonal euxinia, sedimentation rate or the nature of organic matter present.

This barrier to the diffusion of Mo into sulfidic/noneuxinic sediments and the observed distribution of Mo concentrations in such environments should allow us to define a uniquely euxinic Mo signal of ~ 20 ppm or greater. This would allow for the characterization of euxinia where DOP is inconclusive or of Mo limitation where DOP is indicative of euxinia but Mo concentrations are subdued. Additionally, Mo concentrations between 6 and 16 ppm are indicative of sulfidic sediments below an oxic to suboxic water column.

Unexpected denitrification in oxic shelf sands: A consequence of redox dynamics?

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The South Atlantic Bight (SAB) continental shelf seafloor is sandy with elevated permeabilities. Bottom currents, primarily driven by tides, efficiently drive bottom waters into and out of the upper 5-8 cm of the sediments. Because tidal flows and directions alternate with a period of approximately 6 hours, the direction of pore water flow and redox conditions vary on the same time scales. Sun light also reaches the sediment surface supporting significant rates of photosynthesis. Diel variations in photosynthetic oxygen production in the upper 1-2 mm of the sediments add further complexity to the benthic redox dynamics.

To investigate sedimentary remineralization reactions in this dynamic environment, laboratory column reactors were employed to mimic advective pore water transport and diagenesis. Multiple column lengths were employed to yield nominal pore water residence times of 3, 6 and 12 hours. High respiration rates are observed in all columns, consistent with previous estimates based on whole core incubations. Unexpectedly, however, the remineralized nitrogen appears primarily as dinitrogen gas (N_2) as measured directly via inlet membrane mass spectrometry. These direct measurements of N_2 are consistent with measurements of nitrite, nitrate, ammonium, nitrous oxide and dissolved organic nitrogen that reveal little change in these other constituents. Estimates based on the measured oxygen consumption and the Redfield oxygen:nitrogen ratio of planktonic organic matter suggest that most of the regenerated nitrogen is denitrified.

This efficient generation of N_2 is especially unexpected in the 3 and 6 hour residence time columns because the bulk pore waters remain oxic throughout the column reactors. Follow-up experiments in which the influents of the column reactors were amended with ^{15}N labelled nitrate revealed a significant delay in the incorporation of the tracer into the N_2 . These results suggest that the pool of nitrogen that is undergoing denitrification is significantly isolated from the bulk pore waters, at least for periods of days. We speculate that the dynamics of redox conditions in this permeable system have led to the development of this unexpected denitrification pathway.

Denitrification pathways and rates in the sandy sediments of the Georgia continental shelf

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The significance and mechanisms of denitrification in sandy sediments, which comprise 70% of the global shelf area, are not well known. These sediments typically contain low organic matter and dissolved inorganic nitrogen (N) contents and high pore water oxygen concentrations, characteristics that are generally thought unfavorable for supporting heterotrophic denitrification. The possibility of alternative pathways to N_2 , which may not be limited by organic matter content, oxygen, or observed dissolved inorganic N levels, have not been examined in these widespread environments. These alternative pathways include coupled nitrification-denitrification, anammox (anaerobic ammonium oxidation), and OLAND (oxygen-limited autotrophic nitrification-denitrification). Core incubations and isotope pairing techniques were employed to determine pathways and rates of denitrification in the coarse-grained, sandy sediments of the Georgia continental shelf. In these sediments, heterotrophic denitrification was the dominant process for fixed N removal. The alternative pathways (coupled nitrification-denitrification, anammox, and OLAND) were not evident over the 24 and 48-hour timescale of the incubation experiments. Heterotrophic denitrification processes produce $22.8 - 34.1 \mu\text{mole N m}^{-2} \text{d}^{-1}$ of N_2 in these coarse-grained sediments. These denitrification rates are approximately two orders of magnitude lower than rates determined in fine-grained shelf sediments. These lower rates may help reconcile unbalanced marine N budgets which calculate global N losses exceeding N inputs.

A tale of two margins: A comparison of redox and productivity paleo-proxies in sediments off Oman and Peru

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Reconstruction of past changes in environmental redox conditions is valuable for elucidating the interactions and sensitivities between climate change and redox-sensitive biogeochemical cycles. Where suboxic conditions occur in the water column, they are maintained by a combination of poorly ventilated intermediate waters as well as high organic matter (OM) fluxes. However, the sensitivity of suboxia to variations in either is not well known.

We have observed in Oman margin sediments from the Arabian Sea strong variations in denitrification and by inference suboxia in response to climate change at a variety of scales. Across one D-O event examined in detail (Higginson et al., 2004), increased water column denitrification (rising $\delta^{15}\text{N}$) was synchronous with increased suboxia (increased V/Al, Mo/Al and reduced Mn/Al). Productivity intensified at the same time as detected by productivity sensitive metals as well as organic-based proxies suggesting local to regional OM flux as the forcing for variations in suboxic intensity.

On the Peru margin, these relationships at first appear to generally hold. During the latest Holocene, centennial-scale events of sharply increased suboxia as detected by V/Al and Mo/Al correspond to increased productivity as marked by increased Ni/Al and Zn/Al as well total alkenones/Al. During the last deglacial, however, a sharp rise in denitrification marked by high $\delta^{15}\text{N}$ is not synchronous with changes in either sediment redox-sensitive metal concentrations or productivity proxies. In this critical interval, remote change in intermediate water ventilation appears to be the principal forcing.

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Oxygen consumption rates in the shelf and slope sediments of the western Arctic

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Despite the harsh environment in the Arctic, the region supports enough production to fuel substantial benthic respiration rates on the shelves and slopes. Since the Arctic contains approximately 25% of the world's continental shelf, biogeochemical processes that occur in it are thought to be significant though are not well studied due to limitations on accessibility to those areas.

This study examines oxygen consumption rates in the shelf and slopes of the western Arctic. In two cruises in the summer and spring of 2002 and 2004, respectively, profiles of oxygen concentrations in the shelf and slope sediments of the Chukchi and Beaufort Seas were measured by microelectrode. Measurements were made along 4 transects going from shelf to off slope (50-3000 m), each transect having different overlying water characteristics. Oxygen penetration depths ranged from as little as 3 mm in shallow sediments to over 20 cm in deep waters. Oxygen consumption rates calculated from the measured profiles were found to decrease with increasing water depth. Rates varied from about 15 mmol O₂/m² d for the shallow sediments to 1.6 mmol O₂/m² d in the deep. Oxygen consumption rates were found to vary between the two seasons which is not surprising considering the stark dichotomy of the overlying water conditions in the Arctic from spring to summer which result in unequal amounts of organic carbon reaching the sediments. This seasonal variation was more pronounced in the shallow water sediments, probably due to their increased sensitivity, relative to the deep, to the different amounts of organic carbon reaching the sediments in the spring versus the summer. Comparing the rates calculated in this study to rates obtained on the well characterized, very productive Washington state continental margin it was found that the consumption rates in the shallow waters of the western Arctic are generally lower. However, the rates of all four Arctic transects and the WA margin are comparable in the deeper waters.

Oxygen isotope fractionation in marine sediments during respiration

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Net community respiration of aerobic bacteria in sediments is predicted to have an isotopic fractionation factor of $\epsilon = 9\text{‰}$ ($\alpha = 0.991$). This value is smaller than the fractionation determined for free-living aerobic bacteria ($\epsilon = \sim 18\text{‰}$), due to the diffusive limitation inherent to an essentially two-dimensional sedimentary system. Previous measurements of the metabolic oxygen isotope fractionation in suboxic to anoxic sediments showed no oxygen isotope fractionation when the oxygen concentration is reduced to zero at the respiring site.

We present direct measurements of net community oxygen consumption and the isotopic fractionation of oxygen in sediment core incubations. Cores were collected from the Washington State continental margin and the continental margin off the coast of Texas in the Gulf of Mexico. These sites represent a range of depths, bottom-water oxygen conditions, organic carbon rain rates, organic carbon oxidation rates, and sedimentary organic carbon contents. Oxygen consumption ranged from ~ 20 to 40 percent of the initial oxygen concentrations. Oxygen isotopic composition changes over the course of the experiments ranged from 1.7‰ to 5.9‰, corresponding to a fractionation factor of $\epsilon = 6$ to 10‰ (assuming this is a closed system which can be modeled using Rayleigh fractionation kinetics). We hypothesize that the expression of the oxygen isotope fractionation is a function of the degree to which oxygen limits the aerobic respiration rate.

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REE geochemistry of phosphate nodules from the lower Cambrian black shale sequence in the Mufu Mountain of Nanjing, Jiangsu province, China

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Phosphorus is a kind of life element, phosphate sediments probably relate to life events. In South China, phosphate nodules widely occur in early Cambrian black shale sequence in Yangtz platform. In this study, we sampled six phosphate nodules from the Lower Cambrian black shales in Mufu mountain, Nanjing, Jiangsu Province, and analyzed REE concentrations of these nodules from core to rim for each nodule. The general characteristics are as following: 1) Phosphate nodules are symmetrical in geochemistry with total REE concentrations increase from core to rim. The bulk nodule show HREE-enrichment compared with host shale and both are MREE-enriched. The outer layers of nodules are enriched in MREE and P. 2) The inner cores of nodules show seawater-like shale-normalized REE patterns except for Eu anomaly, and the outer layers of nodules display MREE-rich patterns. 3) Positive Eu anomalies are found in all nodules, and as a rule the Eu/Eu* values decrease from core to rim and they negatively correlate with total REE concentrations. The phosphate nodules were likely formed from pore fluids and grew layer by layer during host shales diagenesis. We suggest that both sediment pore water and submarine hydrothermal solution may contribute REE for the nodules. The Eu anomalies and their variations are results of changing proportions between Eu-rich hydrothermal fluid and REE-rich pore water. Alternatively, the changing Eu/Eu* from core to rim may reflect changing redox condition during nodule formation. Phosphorus in phosphate nodules may have solely originated from seawater, coagulated by ferric oxyhydroxides adsorption, enriched in seawater-sediments interface, and deposited in organic-rich basin of deep seawater. The REE characteristics of the nodules provide important insights to early Cambrian ocean environmental changes and submarine hydrothermal activities at that time which produced extreme metal enrichments in the same black shale sequence in the whole South China.

Acknowledgements

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Mn enrichment factors, changes in paleo-redox or source material at Nazca Ridge (ODP Site 1237)

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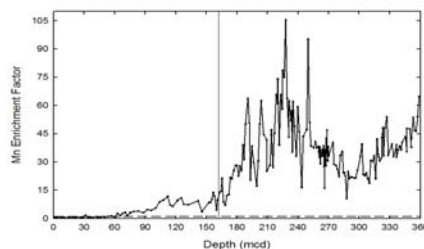
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Observations of sediments at a Nazca Ridge site (Ocean Drilling Program [ODP] Site 1237) revealed an abrupt sediment color change from grayish white in the upper 162 meters composite depth (mcd) to a fairly homogeneous pale brown at greater depth. Site lithology is comprised of siliceous microfossils in the upper 100 mcd dominated by calcareous microfossils in the lower 100 mcd, with no major lithologic change across the color boundary. Interstitial water chemistry indicated a limited influence of organic matter diagenesis, primarily in the uppermost sediments, with no changes in redox character coincident with the color change. This led us to investigate whether there is a change in paleo-redox conditions or a change in source material across this dramatic color change.

Redox sensitive metal enrichment factors (EF), relative to crustal averages, have the ability to describe the redox chemistry of the overlying water and marine sediments at time of burial. Manganese (Mn) EF >1 indicate oxic conditions, while uranium (U) EF > indicates suboxic or anoxic overlying water conditions. Here, we show new records of redox sensitive trace metals Mn and U generated from a Southeast Pacific Nazca Ridge site. These records extend to ~30 Ma over 360 mcd, recording depositional history as the site progressed eastward from a pelagic toward a hemi-pelagic oceanographic setting.

U EF are >1 throughout the sedimentary record and range between 1.38 and 12.4, with a mean value of 4.74. Mn EF, range from 0.63 to 13.8 above the color contact boundary at ~162 mcd jumping to 7.04 to 106 below the boundary (Figure 1). This dramatic change in Mn EF, no change in U EF, and the coincident sharp color contact boundary lead us to conclude that a change in source material, not redox conditions caused this event.

Figure 1: Mn EF versus depth. Dashed horizontal line plotted is the Mn/Ti enrichment relative to $Mn/Ti_{crust} = 1$. Solid vertical line is depth at observed color change.



Denitrification and sulfate reduction in Arctic continental margin sediments

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We have determined sedimentary pore-water nitrate profiles as well as sulfate reduction reduction rates for several cross-margin transects in the eastern Chukchi sea (U.S. Arctic) during Summer 2002 (July-August) and Spring 2004 (May-June). In general, nitrate penetration depths were less than 1 cm for stations shallower than about 200 m but penetration depths increased dramatically as overlying water depth increased. At some of the deepest stations nitrate was present throughout the entire sampling depth (upper 20 cm). There were also significant differences both spatially and temporally. Nitrate penetration generally decreased from west to east and from summer to spring. Nitrate fluxes were calculated from the profiles and varied from about 0.5 to about 0.05 mMoles/m²/d with patterns in rate being inversely correlated with penetration depth. Sulfate reduction rates varied between 2.1 and 0.01 mMoles/m²/d per day; they also decreased with increasing water depth and showed temporal variability. The magnitudes of nitrate reduction rate and sulfate reduction rate as well as their patterns with depth were similar to those those along the productive U.S. west coast for stations near Barrow Canyon (eastern stations) while rates at stations west of Barrow Canyon were much lower. The relatively high rates near Barrow Canyon may be due to off-shelf transport of organic matter through the Canyon.

Quantifying the role of manganese in biotic and abiotic nitrogen cycling

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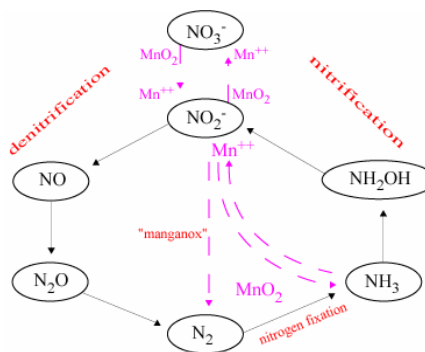
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Motivation

Controversy exists as to the (thermodynamically feasible) role of reduced and oxidized phases of manganese in nitrogen cycling in marine sediments.



Potential roles for Mn⁺⁺ and MnO₂ in the marine nitrogen cycle examined in this study.

Methodology

We investigated the role of manganese in the nitrogen cycle in the Gulf of Mexico. Using an array of inoculations with isotopically-labelled nitrogenous compounds, we examined the role of Mn⁺⁺ as an electron donor in the reduction of NO₃⁻, and the role of MnO₂ as an electron acceptor in the oxidation of both NO₂⁻ and NH₄⁺. Our experiments were specifically designed to distinguish between biotic and abiotic reactions, by using 'live' and 'dead' inoculations in parallel.

Results and Conclusions

Our results suggest a definitive but limited role for MnO₂ and Mn⁺⁺ in both biotic and abiotic nitrogen cycling. Abiotic reactions, where experimentally detected, are generally an order of magnitude slower than their biologically-mediated equivalents.

Effect of bottom water oxygen on phosphorus composition and diagenesis in marine sediments

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Sedimentary organic phosphorus (P) composition was investigated in Effingham Inlet, a fjord located on the west coast of Vancouver Island in Barkley Sound. Solid state ^{31}P nuclear magnetic resonance (NMR) spectroscopy was applied to demineralized sediment samples from sites overlain by oxic and anoxic bottom waters. The two sites were similar in terms of key diagenetic parameters including mass accumulation rate, integrated sulfate reduction rate and bulk sediment organic carbon content. In contrast, P benthic fluxes calculated from sediment pore water profiles were markedly different at the two sites with fluxes of 0.034 and 0.16 mol/m²/y at the oxic and anoxic sites respectively. ^{31}P NMR results show that P-esters and phosphonates are the major organic P species present at the surface and at depth in sediments at both sites. Polyphosphates were only found in the surface sediment of the site overlain by oxic waters.

Varying stability of polyphosphates in microorganisms under different redox conditions may in part explain their distribution as well as differences in P flux between the two sites. The redox sensitive stability of polyphosphates is related to the ability of some microorganisms to store and accumulate P as intracellular polyphosphate granules under aerobic conditions when excess dissolved P is available. If these microorganisms are then exposed to anaerobic conditions, the stored P is utilized and released in dissolved form to the surrounding waters. The presence of abundant phosphate coupled with the availability of oxygen in the water column oxic/anoxic transition zone in Effingham Inlet, provides an ideal environment for polyphosphate accumulation by microorganisms. Presence of polyphosphates in the oxic site sediments suggests that polyphosphate containing microorganisms are transported and sedimented from the redox transition zone. Complete utilization of sedimented polyphosphates and the ensuing release of dissolved P at the anoxic site may both explain their absence in the sediments and partially account for the enhanced benthic P flux at this site.

Elemental cycling in coastal tropical sediments, Saint Lucia, Lesser Antilles: Results from multiple pore water sampling techniques (dialysis, centrifugation, DET, and DGT)

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The rate and vertical distribution of early diagenetic reactions in tropical nearshore sediments often differ from those in temperate or polar climates due to higher sedimentation rates, more constant seasonal temperatures, higher concentrations of secondary weathering products, and higher phytoplankton production rates. These redox reactions involving Fe, Mn, S, and C are important to understand because these reactions largely control the precipitation and dissolution of many mineral phases, including CaCO₃, FeS₂, and possibly some clay phases, as well as influence the mobility of micronutrients or trace metals such as Pb, Zn, Cu, Mo, Ag, Ni, Cr, and As. In this study, we examine the distribution and fluxes of major, minor, and trace elements in modern coastal sediments off the Caribbean island of Saint Lucia using four different pore water solute sampling techniques: dialysis equilibrium (peepers), centrifugation, DET (diffusive equilibrium in thin films), and DGT (diffusive gradients in thin films).

Solutes were determined by ICP, IC, and ICP-MS analyses and DGT concentrations were calculated for trace metals and H₂S from chelex and AgI gels, respectively.

The results show that DET and DGT probes are capable of providing high spatial resolution pore water solute profiles, which can be used to quantify early diagenetic reactions such as iron and manganese reduction, sulfide production, carbonate dissolution, and trace element cycling. Due to the modern areal extent and volume of tropical coastal sediments in the geologic record, these results will help us quantify modern and ancient oceanic elemental budgets.

Geochemical cycling of U, Re and Mo in coastal sediments

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Uranium (U), rhenium (Re) and molybdenum (Mo) are conservative in oxic seawater but are removed from pore waters to sediments under reducing conditions. We examined the geochemical cycling of U, Re and Mo in coastal sediments, which have shallow oxygen penetration depths, through examination of pore water profiles and benthic fluxes.

U and Re removal from pore waters occurred at approximately the depth of maximum pore water Fe²⁺, consistent with Zheng et al. (2002) and Crusius et al. (1996). Mo removal from pore waters occurred several centimeters deeper, suggesting that Mo removal required more reducing conditions. Previous literature suggested that authigenic accumulation of Mo is indicative of either anoxic bottom waters (Adelson et al., 2001) or bottom water oxygen concentrations <3 μM (Zheng et al., 2000). However, bottom water oxygen concentrations were ~300 μM, suggesting that this criterion for Mo authigenesis is too limiting. Flux of organic carbon must be considered when determining conditions necessary for authigenic Mo accumulation.

Calculated benthic fluxes from pore water profiles predict large Mn and Fe and occasional U and Mo fluxes to overlying water. However, much smaller Mn and Fe fluxes to overlying waters are measured using benthic chambers. This difference is most likely due to the coarseness of pore water sampling near the sediment-water interface (0.3 cm). Benthic chamber fluxes for U and Mo are consistently into the sediments and show little seasonal variability.

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