

B52A-0756 1330h POSTER

Identifying Interactions Between Rhizosphere Activity and Leaf Litter Decomposition - a Novel Approach

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Forest soils have received considerable interest due to their potential of storing for the long term carbon fixed by the vegetation above-ground. However, soil processes are complex, and investigations into the interactions between different soil compartments, i.e. roots, litter, and soil organic matter (SOM) are critical to the understanding of carbon stabilisation within forest soils. Recently, forest girdling was successfully applied to stop autotrophic respiration within the soil, thus leaving the heterotrophic CO₂ production as the only remaining flux (Högberg et al. 2001, *Nature* 411, 789-792). The difference in abundance of stable carbon isotopes in litter and soil provides a further opportunity to partition the fluxes measured at the soil surface.

In April 2002, a new girdling experiment has been started in two spruce stands in Germany (young and old). Within this larger experiment, we focussed on the hypothesis that rhizosphere activity in forest soils influence leaf litter respiration. Native litter was replaced with ¹³C-labelled spruce needle-litter in three soil collars located in the experimentally girdled plots and in three collars located in the control plots (non-girdled) of the younger stand (25-years). Reference collars with no litter were established close to the labelled-litter collars for each treatment. Starting four weeks after girdling (May 2002), the soil CO₂ efflux within each collar as well as the $\delta^{13}C$ of the CO₂ emitted from the forest floor were measured at monthly intervals. Owing to the difference in isotopic composition between the litter and the soil, we were able to identify the flux components originating from these two compartments.

Preliminary results show that the difference in CO₂ flux from collars with litter is much higher in the non-girdled plots, indicating an enhancement of litter respiration in the presence of a functional rhizosphere. Isotopic analyses of the soil respired CO₂ show that the additional respiration caused by litter placement originates from two isotopically distinct sources: (a) the needle-litter itself and (b) roots and/or SOM. These results indicate complex interactions between roots, litter and SOM. While root activity stimulates litter respiration, the litter, in turn, seems to stimulate root respiration. Roots and litter together, but not litter alone, may also increase SOM respiration. An isotopic analysis of the soil beneath the collars at the end of the labelled litter experiment (October 2002) will provide further information on the incorporation of litter derived carbon into SOM.

B52A-0757 1330h POSTER

Organic Carbon Export From a Mixed Land Use Watershed

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Changes in land cover and land use for the purpose of agricultural production have long been implicated as significant contributors of nonpoint source pollution and subsequent local and regional water quality problems. In addition to changes in sediment and nutrient export from disturbed ecosystems, carbon export can also be influenced by such changes in land use and land cover. In order to gain insight into the influence of land use on organic carbon export we have initiated a molecular and stable carbon isotope study of dissolved, colloidal and particulate organic matter collected monthly and during storm events from locations in Big Pine Creek watershed, a mixed land use watershed located in West-Central Indiana. Water samples were separated into coarse particulate organic matter, colloidal organic matter, and dissolved organic matter with glass fiber filters and cross flow ultrafiltration. The organic matter from these samples is be-

ing characterized by molecular and stable isotope techniques to determine regional source by the use diagnostic lignin monomer distributions extracted via alkaline cupric oxide oxidation and tetramethylammonium hydroxide thermochemolysis. Ongoing analysis will investigate how differences in land use and/or land management practices may influence the extent and nature of carbon export from terrestrial systems.

B52A-0758 1330h POSTER

Sustainability of Carbon Sequestration in Terrestrial Ecosystems: Theoretical Framework and a Case Study

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A sound understanding of the sustainability of terrestrial carbon (C) sequestration is critical for the success of any policies geared to stabilize atmospheric greenhouse concentrations. This includes the controversial Kyoto Protocol and/or other greenhouse strategies by individual countries. However, the sustainability of C sinks and pools has not been carefully studied with either empirical or theoretical approaches. This study establishes a theoretical framework to define the sustainability based on C influx and residence time (τ). Ecosystem C influx is determined by canopy photosynthetic capacity and leaf area index. The residence time represents the capacity of an ecosystem to store C in plant and soil pools (i.e., the C-storage capacity). The C-sequestration capacity in an ecosystem is jointly determined by the canopy photosynthetic capacity and the C-storage capacity. The C-sequestration capacity is maintained in a future global change scenario only if neither the canopy photosynthetic capacity nor the C-storage capacity is up- or down-regulated. In that case, the future rate of terrestrial C sequestration is primarily determined by environmental forcing functions. The forcing functions could be the rising of atmospheric CO₂ concentration, forest regrowth, woody plant encroachment, and nitrogen deposition.

We applied this framework to the Free-Air CO₂ Enrichment (FACE) experiment in Duke Forest, North Carolina, USA. We estimated C influx with a mechanistic canopy model and residence time via inverse analysis of multiple data sets. Our results indicated that neither canopy photosynthetic capacity nor the C-storage capacity was altered by elevated CO₂ at this forest site. Thus, the current evidence from both experimental observations and inverse analysis suggests that C sequestration in the ecosystem will increase gradually as Ca gradually increases. Nonetheless, the increased C sequestration in terrestrial ecosystems accounts for only a small fraction of anthropogenic C emission.

B52A-0759 1330h POSTER

Sensitivity of Decomposition Rates and Long-term Carbon Sequestration to Modeled Disturbance Scenarios: Implications for National Monitoring Efforts

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Soil systems are central to carbon, water, and nutrient cycles and play a key role in regulating CO₂ exchange in terrestrial systems. While recent advances have been made for measuring plant production, the mechanisms that control the loss of carbon from land are masked by difficulties in detecting and scaling belowground processes. National and international reporting requirements have placed increased emphasis on the development of spatially explicit soil carbon inventories based on monitoring changes in major soil reservoirs. Although this inventory approach provides critical baseline information, the ecological significance of this soil carbon ultimately depends upon the level of chemical and physical protection, the response of the soil system to disturbance, and the temporal and spatial scales of interest.

In this paper, we model the sensitivity of carbon storage estimates to differing assumptions of decomposition and disturbance response using data from the USDA Forest Services Forest Inventory and Analysis (FIA) Program. The FIA soil indicator program represents the only nationally consistent source of forest soil monitoring data in the United States and forms the basis for national reporting on the Montreal Process Criteria and Indicators of Sustainable Management. A

mass-balance model of long term soil carbon dynamics is used to address the following questions: (1) how sensitive are soil carbon inventories to current assumptions of inputs, turnover, and disturbance response; (2) which soil processes have the greatest influence on C storage over the time scales relevant to land use policies and how can we best monitor these processes; (3) what are the critical data gaps limiting the use of inventory data in regional and global carbon models.

B52B MCC: 132 Friday 1330h

Merging Molecular Techniques and Genomics With Biogeochemistry II (joint with H, OS)

Presiding: M E Dolan, Oregon State University; A Reysenbach, Portland State University

B52B-01 1335h INVITED

Applications of Synchrotron X-ray Absorption Spectroscopy to Biogeochemical Speciation, Fate, and Remediation of Metal and Metalloid Contaminants in Natural Settings

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Synchrotron X-ray characterization methods, particularly X-ray absorption and diffraction methods, are valuable tools for the analysis of contaminated materials and offer opportunities for designed remediation. These techniques have moved beyond the analysis of model systems alone and can be used to characterize element speciation in solid and aqueous natural samples. Studies of redox-sensitive elements subject to biotically induced changes in oxidation state are particularly amenable to analysis by XAS, XANES and EXAFS can aid in identifying the redox state and chemical speciation of metal and metalloid contaminants, which determines their bioavailability, toxicity, and mobility in the environment. As such, these spectroscopic methods can be integrated with established chemical and physical analyses to contribute to the overall understanding of reaction and transport in contaminated systems, and used to design intelligent remediation strategies. A particular challenge in applying XAS to real systems lies in the identification and quantification of particular species or phases within complex mixtures such as soils, sediments, and reactive barriers. With proper theoretical and experimental calibration, spectral analyses can yield insight into molecular biogeochemical processes that control contaminant uptake and release. Examples from recent studies include elucidation of coupled changes in arsenic, iron, and sulfur speciation responsible for the natural attenuation of high levels of arsenic in a shallow aquifer, and identification of reaction products in experiments designed to assess remediation and removal methods for arsenic in groundwater using zero-valent iron. Integration of XAS and other synchrotron methods with molecular biology approaches such as nucleotide probes directed against r-RNA targets hold promise for probing spatial relationships and chemical gradients in microbial-mineral systems that control contaminant cycling.

B52B-02 1350h INVITED

Compound Specific Isotope Analysis: A Novel Method of Assessment and Quantification of In Situ Remediation Potential

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Compound Specific Isotope Analysis (CSIA), or the characterization of stable carbon and hydrogen isotope compositions of individual contaminant compounds dissolved in groundwater, provides a novel method for investigation of degradation and remediation potential at contaminated sites. For organic contaminants such as chlorinated solvents and petroleum hydrocarbons, degradation can involve large and reproducible kinetic isotope effects, producing systematic changes in the delta ¹³C and 2H values of the residual contaminant. Examples from recent field applications will demonstrate that during both biological and chemical

degradation, the light (12C, 1H) versus heavy isotope (13C, 2H) containing bonds are preferentially degraded, resulting in isotopic enrichment (fractionation) of the residual contaminant. For instance, large carbon isotope enrichments in the residual contaminant of several permil to greater than 10 permil have been observed during degradation of PCE, TCE and petroleum hydrocarbons. In addition, characterization of the isotopic composition of both the degrading parent compound and daughter products indicate that when initially produced, daughter products are more isotopically depleted in the heavy isotope than the parent compound, reflecting the preferential biodegradation of light isotope containing molecules. The daughter products then begin to show the same characteristic isotopic enrichment trends however, as they themselves undergo degradation. VC and cisDCE in particular can show very large carbon isotope fractionation effects, with up to 40 permil and 30 permil enrichment in 13C in the residual contaminant, respectively. Even larger fractionation is often observed when delta 2H values are measured, due to the preferential rate of degradation for the light 1H-containing molecules. In many cases, stable isotope fractionation during degradation can be modelled by a simple Rayleigh distillation model that relates the change in observed stable isotope compositions to the extent of degradation. Stable isotope analysis can therefore provide a direct indication of the effects of degradation on specific contaminants, as well as a novel independent means to quantify the extent of degradation and estimate degradation rates.

B52B-03 1405h INVITED

Monitoring in Situ Anaerobic Alkylbenzene Biodegradation Based on Mass Spectrometric Detection of Unique Metabolites or Real-Time PCR Detection of a Catabolic Gene

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Monitored natural attenuation (MNA) can be a cost-effective and viable approach for remediation of hydrocarbon-contaminated groundwater. However, regulatory acceptance of the approach is often contingent on monitoring that can convincingly demonstrate the role of microbial degradation. Recent advances in anaerobic hydrocarbon biochemistry, analytical chemistry, and molecular biology have fostered the development of powerful new techniques that can be applied to MNA of BTEX (benzene, toluene, ethylbenzene, and xylenes). Here we report two independent methods that have been developed to monitor in situ, anaerobic biodegradation of toluene and xylenes.

A method has been developed for rapid, sensitive, and highly selective detection of distinctive indicators of anaerobic alkylbenzene metabolism. The target metabolites, benzylsuccinic acid (BS) and methylbenzylsuccinic acid (MeBS) isomers, have no known sources other than anaerobic toluene or xylene degradation; thus, their mere presence in groundwater provides definitive evidence of in situ metabolism. The method, which involves small sample size (<1 mL) and no extraction/concentration steps, relies on isotope dilution liquid chromatography/tandem mass spectrometry (LC/MS/MS) with selected reaction monitoring. Detection limits for benzylsuccinates were determined to be ca. 0.3 µg/L and accuracy and precision were favorable in a groundwater matrix. The LC/MS/MS method was used to characterize geographic and temporal distributions of benzylsuccinates in an anaerobic, hydrocarbon-contaminated aquifer. BS was never detected and MeBS isomers were detected in the three wells with the highest concentrations of BTEX; MeBS concentrations ranged from <0.3 to 205 µg/L. A strong linear correlation was found between concentrations of total MeBS isomers and their parent compounds, xylenes.

A monitoring method based on real-time Polymerase Chain Reaction (PCR) analysis has been developed to specifically quantify populations of anaerobic methylbenzene-degrading bacteria in aquifer sediment. The method targets a catabolic gene (*bssA*) associated with the first step of anaerobic toluene and xylene degradation. The method proved to be sensitive (detection limit ca. 5 gene copies) and had a linear range of > 7 orders of magnitude. In microcosm experiments involving toluene degradation under denitrifying conditions, population trends were generally consistent with observed toluene degradation activity. In the microcosms with the most rapid toluene degradation, numbers of *bssA* copies increased 100- to 1000-fold over the first four days of incubation, during which time most of the toluene had been consumed. These results were supported by slot blot analyses with unamplified DNA and by cloning and sequencing of putative *bssA* amplicons.

B52B-04 1420h INVITED

Linking Diversity and Stable Isotope Fractionation in Ammonia-Oxidizing Bacteria

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Ammonia-oxidizing bacteria play a key role in the regeneration of nitrate (NO₃) and the production of nitrous oxide (N₂O) in many marine, estuarine, and terrestrial ecosystems. While isotopic ratios (¹⁵N/¹⁴N) of dissolved inorganic nitrogen pools (NH₄⁺ and NO₃) can serve as *in situ* tracers for overall nitrification activity, genetic characterization of bacterial communities can provide information about the diversity and relative abundance of specific groups of ammonia-oxidizers. An important question facing microbial ecologists is how diversity in gene or protein sequences is reflected in diversity in biogeochemical activity. Here we investigate the link between similarity in amino acid sequence for ammonia monooxygenase (AmoA) and its isotopic discrimination (ε_{AMO}) for B-subdivision ammonia-oxidizing bacteria. Isotope effects for ammonia-oxidation were measured for 5 cultured nitrifier strains. A 20 permil range in isotope effects was observed among these nitrifiers, which could not be explained by differential rates of ammonia oxidation, transport of NH₄⁺, accumulation of NH₂OH, or N₂O production among the strains. The major similarities and differences observed in ε_{AMO} are, however, paralleled by similarities and differences in AmoA amino sequences from these organisms. These results suggest that combining genetic and stable isotopic tools may provide complementary information regarding the activity of particular groups of ammonia-oxidizers in the environment.

B52B-05 1435h

Study of Lateral Gene Transfer in an Acid Mine Drainage Community Enabled by Comparative Genomics

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Lateral gene transfer (LGT) is thought to play a crucial role in the ecology and evolution of prokaryotes. We are investigating the role of LGT in an acid mine drainage community hosted in a pyrite-dominated metal sulfide deposit at the Richmond mine at Iron Mountain, CA. Due to biologically-mediated pyrite dissolution, the prevailing conditions within the mine are extremely low pH (< 1.0), very high ionic concentrations (molar concentrations of iron sulfate and mM concentrations of arsenic, copper and zinc), and moderate to high temperatures (30 to >50 C). These conditions are thought to largely isolate the community from potential external gene donors since naked DNA, phage and prokaryotes native to neutral pH habitats do not persist at pH <1.0 precluding an external influx of genes by transformation, transduction and conjugation, respectively. Microbial communities exist in several distinct habitats within Richmond mine including biofilms (subaqueous slime streamers and subaerial slimes) and cells attached directly to pyrite granules. This, however, belies an unusual simplicity in community composition. All communities investigated to date comprise only a handful of phylogenetically distinct organisms, typically dominated by the iron-oxidizing genera *Leptospirillum* and *Ferroplasma*. We have undertaken a community genomics analysis of a subaerial biofilm dominated by a *Leptospirillum* population to facilitate the study of LGT in this type of environment. The genome of *Ferroplasma acidimanus* fer1, a minor component of the target community (but a major component of other Richmond mine communities), has been sequenced. Comparative genome analyses indicate that *F. acidimanus* and the ancestor of two acidophilic *Thermoplasma* species belonging to the Euryarchaeota have traded many genes with phylogenetically remote acidophilic *Sulfolobus* species (Crenarchaeota). The putatively transferred sets of *Sulfolobus* genes in *Ferroplasma* and the *Thermoplasma* ancestor are distinct, suggesting independent LGT events between organisms living in

the same, and adjacent habitats. In both cases, however, the majority of transferred genes are involved in metabolism, particularly energy production/conversion and amino acid transport/metabolism. The lack of genes transferred from the (sequenced) genomes of other prokaryotes is consistent with the hypothesis that extreme acidophiles have limited access to genes from organisms outside their ecotype. To date, no *Sulfolobus* species have been detected at Iron Mountain, suggesting two possibilities to explain the observed pattern of putatively transferred genes to *Ferroplasma* from *Sulfolobus*: 1) *Sulfolobus* is present at Iron Mountain but in regions currently inaccessible to sampling and/or 2) the transfers occurred prior to introduction of *Ferroplasma* into the current geological setting. As community genome data become available, we should be able to more accurately determine the extent and character of LGT between members of this extremely acidophilic community.

B52B-06 1450h INVITED

Archaeal Lipid Genes: Clues to Life in Acid and the Evolution of Membranes

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Microorganisms living in acid mine drainage environments face extraordinary challenges. Acid-loving archaea such as *Ferroplasma acidimanus* maintain pH gradients of 4 to 5 pH units across their membranes and thrive in hot, extremely low pH (0-1), metal-rich, solutions. New lipid analyses for two extremely acidophilic archaea, *F. acidimanus* and *F. acidiphilum*, reveal that all known archaeal acidophiles have cell membranes composed primarily of tetraether-linked lipids. Because tetraether lipids assemble in rigid monolayers that exclude protons and metals, we suggest that tetraether synthesis genes are essential for archaeal survival in acid.

Fusion of two diether-linked lipids to form a tetraether-linked lipid is a distinctive biochemical reaction with no analogy in bacteria and eukaryotes. In addition to archaeal acidophiles, tetraethers are present in members of every archaeal lineage except halophiles. Genes responsible for tetraether synthesis and subsequent biochemical steps which "tune" membrane lipid properties in response to environmental changes have not been identified to date. Comparative genomic analyses using the newly completed genome of *F. acidimanus* and available genomes from Bacteria, Archaea and Eukarya have generated candidate tetraether synthesis genes found only in archaea. Because tetraether-linked lipids are advantageous for acid-loving and possibly also for heat-loving archaea, the phylogeny of these genes has the potential to shed new light on role of hot, acid environments in early evolution.

B52B-07 1505h

From Genomes to Biomes: Understanding Biogeochemical Processes via Environmental Genomics

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Microbial life regulates most of the key redox transformations that occur in natural biogeochemical cycles. Genomics-enabled approaches in microbial ecology can now significantly advance current knowledge of the genome content, diversity, population biology and evolution in natural microbial ecosystems. Cultivation-independent genomic approaches provide direct, generic access to the genome content, functional diversity, and population biology of naturally occurring

microbial communities. One advantage of applying genomic approaches is that they are not reliant on a priori assumptions about the specific organisms, biochemical pathways, or biogeochemical processes that are present and active in any particular habitat or community. Therefore, the community composition, genetic character, and biochemical pathways present can be evaluated in a more unbiased fashion. Discoveries concerning the genetic properties of uncultivated microbes, as well as novel genes and biochemical pathways, are now resulting from environmentally-oriented genomic studies. Examples include the discovery of novel phototrophs in marine plankton, and the genetic dissection of uncultivated methane-oxidizing consortia from anoxic deep-sea methane seeps. Results from these early studies indicate that genomic dissection of naturally occurring microbes is extremely useful for characterizing the microorganisms, biochemical pathways and biogeochemical processes that occur in natural environments.

URL: <http://www.tigr.org/tdb/MBMO/>

B52C MCC: 132 Friday 1535h

Life and the Evolution of the Earth System: Processes and Theories (*joint with H, OS, GC, PP*)

Presiding: A Kleidon, University of Maryland; **S H Schneider**, Stanford University

B52C-01 1545h INVITED

A Metric to Guide the Search for Biosphere-Scale Principles

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Various metrics have been proposed to measure large-scale structure at the biosphere level, including metrics of mass (such as primary productivity) and energy (such as entropy). Here I suggest a metric called the cycling ratio. It is defined, for any system, as the ratio of the flux of any specified element into the photosynthesizers relative to the flux of that element into the system across its boundaries. In general, the ratio is greater than one because of coordinated processes in which the wastes from some life forms become the food of others. The cycling ratio can be applied across scales of space and time, and across biologically-essential elements. For space, I will show data from Hubbard Brook Forest to the biosphere. For time, I will sketch evidence for the growth of the cycling ratio of carbon over Earth history. And I will compare the cycling ratio for different elements at various scales. The cycling ratio could be used to help develop and focus questions about the coevolution of life and the environment, because it measures the amplification of photosynthesis within a system, compared to the magnitude of photosynthesis if limited to an amount equal to the rate of external supply of an essential element.

B52C-02 1605h

Biogeophysical Effects and the Production of Entropy by the Earth System

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The Earth is an open thermodynamic system. Incoming solar radiation of low entropy is subsequently converted by diabatic processes into a flux of terrestrial radiation associated with relatively higher entropy. It has been suggested that physical processes within the climate system, such as polar heat transport or vertical exchange processes in the atmosphere, act to maximize entropy production. Here I apply these thermodynamic considerations to the overall climatic effect of terrestrial vegetation. Terrestrial vegetation directly affects land surface functioning, such as the absorption of solar radiation and the rate of evapotranspiration. With climate model simulations of extreme vegetation settings, a "green planet" and a "desert world", I investigate how terrestrial vegetation affects the entropy production budget of the Earth and whether the overall biogeophysical effect can be described as such an entropy-maximizing process. The results are discussed in the context of the Gaia hypothesis, which states that the Earth system is regulated by and for the biosphere.

B52C-03 1620h INVITED

Methane Greenhouses and Anti-Greenhouses During the Archean Era

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Climate and life are coupled today through the biogeochemical carbon cycle, but they may have been even more tightly coupled in the distant past when atmospheric O₂ levels were lower. The finding of mass-independently fractionated S isotopes in Archean rocks confirms that pO₂ was very low, probably <10-13 times the present level, prior to 2.3 Ga (1). The Sun was also some 20 percent less luminous at this time (2). High CO₂ levels were initially proposed to solve this 'faint young Sun problem' (3); however, these levels are in conflict in data from paleosols (4). CH₄ is an alternative greenhouse gas which could have kept the Archean climate warm if present at concentrations of 0.01-0.1 percent by volume (5).

The primary source of methane is biological. CH₄ is produced by methanogenic bacteria that today live in anaerobic environments such as the intestines of ruminants and the water-logged soils underlying rice paddies. During the Archean, however, methanogens should have been widespread, and the methane they produced would have had a long photochemical lifetime, around 10,000 years (6). Most methanogens are thermophiles or hyperthermophiles, and those which are more thermophilic have shorter doubling times than those that prefer cooler temperatures. This suggests that a positive feedback loop may have existed, whereby methanogens warmed the climate by releasing CH₄, which in turn promoted the proliferation of faster-growing methanogens. This positive feedback would have been halted, however, once the ratio of CH₄ to CO₂ in the atmosphere exceeded unity. At this point, polymerization of CH₄ by solar UV radiation would have caused the formation of an organic haze layer similar to that observed today on Titan. Such a haze layer would have cooled the climate by creating an 'anti-greenhouse effect.' This creates an overall negative feedback loop that may have been responsible for maintaining a stable Archean climate. The rise of O₂ at 2.3 Ga disrupted this equilibrium and may well have triggered widespread, possibly Snowball, Huronian glaciation.

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B52C-04 1640h

The Peroxy Challenge to Early Life

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The development of aerobic metabolism was one of the most important breakthroughs in evolution. But the early Earth was anaerobic, with most researchers today attributing the build-up of free O₂ to oxygenic photosynthesizers. This reasoning is problematic because photosynthesis invariably produces oxygen radicals as by-products or intermediates. Known collectively as reactive oxygen species, ROS, these radicals damage DNA, damage membranes, and inactivate essential enzymes. In addition, molecular data on the evolution of cytochrome oxidase suggest that early organisms must have learned to detoxify ROS prior to the evolution of aerobic metabolism and oxygenic photosynthesis. A possible way out of this dilemma comes from a study of igneous and high-grade metamorphic rocks, which indicates that a small but significant fraction of the oxygen anions in their minerals exists in the 1 state, forming peroxy links of the type O₃Si-O-SiO₃ (J. *Geodynamics* 33, 543-570, 2002). Water hydrolyzes these peroxy links to hydrogen peroxide,

H₂O₂. As a result, microorganisms that attach themselves to mineral grains will be exposed to a constant trickle of ROS from the production of H₂O₂. We propose the following scenario: Though the overall conditions on the early Earth were anaerobic, conditions at microsites were not. The hydrolysis of peroxy links in minerals to hydrogen peroxide at the rockwater interface was biochemically challenging for any microbes living in intimate contact with rock surfaces. The generation of ROS placed the microbes under evolutionary stress to develop biochemical defenses against the potentially lethal effects of ROS radicals. Only after these enzymatic defenses were in place, oxygenic photosynthesizers were able to develop and increase the O₂ partial pressure in the Earth's atmosphere to a high level.

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Kerogen Characterization of Microfossils in Precambrian Cherts: Evidence for Biogenicity

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Currently, much of our oldest evidence of life on this planet has been called into question. It is not enough for a possible microfossil to have bacterial morphology. In addition, it must also be composed of material with an unquestionably biogenic origin. Once an organism dies, the carbon it contains is altered through diagenesis and metamorphism. Most organic material is removed or remineralized, but insoluble amorphous carbon, known as kerogen, may remain. With additional heating and pressure, this kerogen is transformed into graphite, eliminating the structural biosignature of the material. No known biological process creates graphite as a product. Oxides, which form on the external surface of bacterial cell walls, may also remain after fossilization. Many microfossils are defined not by kerogen but by arrangements of small iron or manganese oxide crystals, even though kerogen may still be associated with them. Cherts from Mink Mountain locality of the Gunflint Formation (2.0 Ga) contain black, brown, and red filaments composed of both hematite crystallites up to 1 μ m and kerogen. The amount of kerogenous material determines the color of the microfossil. Those with little associated kerogen appear red, the color of hematite, while those with much associated kerogen appear black. Brown microfossils are the result of remnant carbon with little or no hematite. Kerogen is also found abundantly outside of microfossils and may possibly be the remains of ancient biofilm.

The crystallinity of carbon, grading from amorphous carbon to graphite, can be measured via a variety of methods, including X-ray diffractometry (XRD), Raman spectrometry, high-resolution transmission electron microscopy (HRTEM), and electron energy loss spectrometry (EELS) in TEM. However, EELS may be the best method when dealing with small patches of carbon associated with microfossils, especially if high-resolution imaging is not possible. Information about the crystallinity is given by the morphology of the near edge fine structure of the carbon K-edge. Specifically, the relative intensities of smaller structures on the σ^* peak and the width of the σ^* peak both increase with increased graphitization. EELS analysis has been performed on cherts from Schreiber Beach, which contains typical, well-accepted microfossils of the Gunflint Formation (2.0 Ga). These microfossils are composed entirely of kerogen in a matrix of microcrystalline quartz. The spectrum of this kerogen is very similar to that of amorphous carbon.

The biogenicity of carbon structures within the Apex Chert (3.5 Ga) is in contention. Raman spectra of these structures have been interpreted as either representing highly disordered graphite (Brasier et al. 2001) or partially graphitized kerogen (Schopf et al. 2001). The former implies an abiogenic origin, whereas the latter implies a biogenic origin. We will use EELS and HRTEM to determine the crystallinity of this carbon in the Apex Chert.