

on short time scales. This study is a first step toward making such an assessment. Observations of instantaneous rain rate from TRMM and SSM/I polar-orbiting satellites are averaged over model grid cells with horizontal spacing of approximately 200km, which is consistent with global scale atmospheric simulations used for climate change prediction. The grid cells are grouped by geographic region (such as tropical, extratropical, land and ocean) and sufficient satellite overpasses are collected to construct distribution functions for each region of the frequency of occurrence of rain rates ranging from less than 0.1 mm/hr to greater than 10 mm/hr. The observed frequency distributions are compared with output from a coincident simulation of the GFDL atmospheric general circulation model. Corresponding simulated frequency distribution functions are constructed from snapshots of rain rate from individual time steps of the model, which are sufficiently sampled to capture the full diurnal variability of precipitation. Excessive drizzle associated with difficulty parameterizing cumulus convection is commonly observed in modern GCMs. The extent of this problem is examined quantitatively in this study and the sensitivity of such problems to the formulation of cumulus convection is discussed.

U52B MCC: 3001-3003 Friday 1340h

Evolution of Biogeochemical Cycles I

Presiding: P Falkowski, Institute of Marine and Coastal Sciences, Rutgers University; M New, NASA Headquarters

U52B-01 1340h

Carbon Dioxide Cycling and a Methane Greenhouse on Ancient Earth

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The continental cycle of silicate weathering and metamorphism dynamically buffers atmospheric CO₂ and climate. Feedback is provided by the strong temperature dependence of silicate weathering. Hydrothermal alteration of oceanic basalts can also dynamically buffer CO₂. The oceanic cycle links the surface to the mantle. Feedback is provided by the dependence of carbonization on dissolved carbonates in sea-water. The oceanic cycle has no thermostat. Currently the continental cycle is more important, but early in Earth's history, especially if heat flow were higher than it is now, more vigorous plate tectonics would have made the oceanic cycle dominant. We find that CO₂ greenhouses thick enough to defeat the faint early Sun are implausible and that, if no other greenhouse gases are invoked, very cold climates are expected for much of the Proterozoic and the Archean. This prediction for the most part flies in the face of evidence that early Earth was warm. We favor biogenic methane as the chief supplement to CO₂. High methane abundances (hundred to thousands of ppm) are expected given methane's current biological source and an anoxic atmosphere. Methane is a likely primary product of the advent of oxygenic photosynthesis. To first approximation methane and oxygen enter the atmosphere in stoichiometric proportions. Mostly the methane and oxygen react with each other, but a small fraction of the oxygen reacts with rocks or with volcanic or metamorphic gases. This it is methane that accumulates first. High methane abundances in turn affect the oxidation state of the Earth because they facilitate hydrogen escape. Possible consequences of the irreversible oxidation of the Earth include the oxygenation of the atmosphere.

U52B-02 1355h

The use of mass-independent and mass-dependent isotope fractionations to study the sulfur cycle

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The inclusion of $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ data with $\delta^{34}\text{S}$ data is providing a new perspective on the evolution of Earth's sulfur cycle. Two types of sulfur isotope fractionations have been observed in the geologic record, mass-independent isotope fractionations and mass-dependent isotope fractionations. Mass-independent isotope effects have been reported in some of Earth's oldest rocks, present-day atmospheric aerosol samples, and in some volcanic ash layers in ice cores (c.f., Savarino et al. year, 2002 AGU Fall meeting). These mass-independent isotope signatures have been used both to provide insight into the atmospheric sub-cycle and also as a tool to trace the movement of sulfur through other parts of the global sulfur cycle. Mass-dependent isotope effects are responsible for most of the very large range of $\delta^{34}\text{S}$ fractionations that are observed in the geologic record. The ability to identify different types of mass-dependent isotopic fractionations by using $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ data can provide a means of differentiating between different types of biological and abiological signatures in the geologic record. We will discuss the developing framework for evaluating these mass-dependent isotopic fractionations and their range of potential applications (see also Johnston et al. 2003 AGU Fall meeting).

U52B-03 1410h

Implications of Multiple Sulfur Isotopes for Biological Systems

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The major isotopes of sulfur ($\delta^{34}\text{S}$) provide a valuable tool to study the evolution and dynamics of ancient biological systems. We recently described the additional information that evidence from $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ can provide for our understanding of metabolic pathways in geological environments (Farquhar et al., 2003). The application of the minor isotope system of sulfur arises because recent advances in analytical techniques allow us to measure different mass-dependent fractionation relationships that are predicted for different types of sulfur metabolisms (disproportionation vs. dissimilatory reduction). Here we report on the progress of experiments to measure the mass-dependent fractionation relationships for a variety of sulfur metabolisms and also the implications of our findings for study of the sulfur cycle. Our results may provide a test for a hypothesis that an apparent change in $\delta^{34}\text{S}$ values during the Neoproterozoic reflected a shift in dominant metabolic process from sulfate reduction to sulfur disproportionation (Canfield and Teske, 1996; Canfield, 2000). This shift in dominant metabolic process has been interpreted as providing evidence for the oxidation state of the ocean and atmosphere at this time.

U52B-04 1425h

Oxygen Isotopes in Marine Sulfate: Reassessing the Sulfur Cycle Over the Past 10 Million Years

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Sulfate plays an important role in the modern ocean, serving as the primary oxidant for much of the organic matter and nearly all the methane produced in ocean sediments, yet the biogeochemical cycle of marine sulfate is assumed to be relatively stable with a long residence time of over 10 million years. Nearly all investigations into the long term dynamics of the marine sulfate cycle have focused on the sulfur isotopes of reduced sulfate deposits, primarily pyrite, and most have concluded that marine sulfate concentrations were low in the Archean, increased in the Proterozoic to modern values, and have remained more or less unchanged through much of the Phanerozoic. Because of the widely varying oxygen isotopic composition of the various sources and sinks of sulfate to the ocean, we suggest that temporal variations in the oxygen isotopes of marine sulfate may provide a closer look at the dynamics of the biogeochemical sulfate cycle. We present a continuous record of oxygen isotopes in marine sulfate measured in marine barite over the last 10 million

years. Large shifts in the oxygen isotopic composition of marine sulfate, including a decrease of 6 per mil over the past 2.5 million years, indicate that the marine sulfate cycle is far more dynamic than previously thought. We use these measurements with a numerical model to explore changes in marine sulfate over the past 10 million years. Although many parameters in the sulfate budget are not well constrained, we identify several scenarios which can explain the observed pattern of oxygen isotopic variations. We suggest that changes in the sulfate cycle are linked closely to changes in sulfate reduction and sulfide reoxidation on continental shelves, which were affected by the periodic glaciations of the Plio-Pleistocene.

U52B-05 1440h

Biomarkers Indigenous to Late Archean Rocks

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Two new lines of evidence support the authenticity of molecular fossils in late Archean rocks of the Hamersley Province, Western Australia. Specifically, they support 1) a syngenetic relationship between the kerogen and extractable biomarkers, and 2) an indigenous relationship between extractable compounds and the host rocks. Carbon skeletons released from kerogen via high-pressure hydrolysis match those found in associated extracted bitumen. Biomarker ratios indicate less mature steranes and terpanes (i.e. hopanes and tricyclic terpanes) are embedded in the kerogen matrix as compared to the highly mature steranes and terpanes in the extracts, which is similar to findings in other hydrolysis experiments. Lithology-associated variations in biomarker distributions are noteworthy and suggest environmental settings are associated with differing biotic ecosystems. The evidence reported here confirms the 2.7 Ga antiquity of diverse biosynthetic pathways. Molecular data, together with isotopic data, indicate aerobic and anaerobic respiration pathways were fundamental to the complex microbial biogeochemistry of the late Archean. The biomarkers in these rocks support an early radiation of the three domains of life and radiation within the bacteria, such that clades of cyanobacteria, green sulfur bacteria, and proteobacteria had been established.

U52B-06 1455h

The Origin of Sterol Biosynthesis: A Time-Point for the Evolution of Eukaryotes and the Presence of O2

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The evolution of sterol biosynthesis is of critical interest to geoscientists as well as to evolutionary biologists. The first enzyme in the pathway, squalene monooxygenase (Sqmo), requires molecular oxygen (O₂), suggesting that this process post-dates the evolution of Cyanobacteria. Additionally, the presence of steranes in ancient rocks marks the suggested time-point of eukaryogenesis(1). Sterol biosynthesis is viewed primarily as a eukaryotic process, and the frequency of its occurrence in bacteria long has been a subject of controversy. In this work, 19 protein gene sequences for Sqmo from eukaryotes were compared to all available complete and partial prokaryotic genomes. Twelve protein gene sequences representing oxidosqualene cyclase (Osc), the second enzyme of the sterol biosynthetic pathway, also were examined. The only unequivocal matches among the bacteria were the alpha-proteobacterium, *Methylococcus capsulatus*, in which sterol biosynthesis already is known, and the planctomycete, *Gemmata obscuriglobus*. The latter

species contains the most abbreviated sterol pathway yet identified in any organism. Experiments show that the major sterols in Gemmata are lanosterol and its uncommon isomer, parkeol. In bacteria, the sterol biosynthesis genes occupy a contiguous coding region and may represent a single operon. Phylogenetic trees show that the sterol pathway in bacteria and eukaryotes has a common ancestry. Gemmata may retain the most ancient remnants of the pathway's origin, and it is likely that sterol biosynthesis in eukaryotes was acquired through gene transfer from bacteria. However, this work indicates that no known prokaryotes could produce the 24-ethyl steranes found in Archaean rocks(1). Therefore these compounds remain indicative of the presence of both eukaryotes and O₂ at 2.7 Ga. 1. J. J. Brooks, G. A. Logan, R. Buick, R. E. Summons, (1999) Science 285, 1033-1036.

U52B-07 1510h INVITED

Bacterial Bolsheviks: PS II and the Evolution of the Oxygenic Revolution

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After the rise of life itself, the most radical transformation of Earth's biogeochemical cycles was the transition from an anoxic to an oxic world. Though various studies have suggested O₂ made its first bulk appearance in the atmosphere some time between 3.8 and 2.1 Ga, virtually all analyses agree the production of large quantities of free O₂ was triggered by the evolution of oxygenic photosynthesis. We suggest the oldest strong geological evidence for O₂ is the 2.22 Ga Kalahari Mn member of the Hotazel BIF (1), as in the oceans only free O₂ can oxidize soluble Mn(II) into insoluble Mn(IV). Some have argued, however, that oxygenic cyanobacteria had originated by 2.7 Ga. The ~500 Myr "gap" has often been interpreted as the timescale for gradual evolutionary improvement of the O₂-generating system. Biochemical and genomic analyses of photosynthetic bacteria indicate that photosystems I and II, which operate together in cyanobacteria, had a long history of parallel development. Green sulfur bacteria and heliobacteria use PS-II, while green non-sulfur and purple bacteria use PS-I; none can use H₂O as an electron donor. Recent genetic analyses show lateral gene transfer was rampant among photosynthetic lineages (2). Moreover, extant cyanobacteria shut down PS-II in the presence of an alternative electron donor like H₂S. This suggests PS-I and PS-II came together with their functions intact. Hence, most debugging' of the two systems predates their merger in the ancestor of modern cyanobacteria. The time interval between the lateral transfer events and the evolution of oxygenic photosynthesis could thus have been geologically short. We suggest the ~500 Myr "gap" may result from misinterpretations. The presence of oxygenic photosynthesis is uncertain before the deposition of the Hotazel formation, in the aftermath of the Makganyene glaciation (1). A simple model of nutrient and reductant fluxes argues that, once triggered, the oxygenation of a reducing surface environment warmed by a CH₄ greenhouse (3) should occur fairly rapidly, within ~ 10 My. The trigger requires both the evolution of cyanobacteria and sufficiently high nutrient (mainly P) fluxes to allow O₂ production to overwhelm reductant fluxes. P flux into the oceans in glaciated worlds correlates with increased continental weathering during glacial intervals (4). Thus, were cyanobacteria present during the Huronian glaciations, which predate 2.22 Ga (5), these glaciations should have triggered the oxygenation event. Instead, the oxygenation event seems to correlate with the Makganyene glaciation, at 2.22 Ga (6). The appearance of red beds in the Upper Timeball Hill formation directly underlying the Makganyene diamictite supports this interpretation. As would be expected from a glaciation associated with the destruction of a CH₄ greenhouse, paleomagnetic data indicate the Makganyene glaciation was a global Snowball event (7). Cyanobacteria appear to have evolved in the short interval between the Huronian glaciations and the Makganyene glaciation. The lengthy delay between the earliest life on Earth and the appearance of cyanobacteria suggests that the oxygenic revolution was a fairly low probability event; planets with oxygenic biospheres may be quite rare. 1. J. L. Kirschvink et al., PNAS 97, 1400-1405 (2000). 2. J. Raymond et al., Science 298, 1616-1620 (2002). 3. A. A. Pavlov et al., JGR 105, 11981-11990 (2000). 4. K. B. Föllmi, Geology 23, 503-506 (1995). 5. S. R. Noble, P. C. Lightfoot, Can. J. Earth Sci. 29, 1424-1429 (1992). 6. D. H. Cornell et al., Precamb. Res. 79, 101-123 (1996). 7. D. A. Evans et al., Nature 386, 262-266 (1997).

U52C MCC: 3001-3003 Friday 1600h

Evolution of Biogeochemical Cycles II

Presiding: P Falkowski, Institute of Marine and Coastal Sciences, Rutgers University; M New, NASA Headquarters

U52C-01 1600h

The Co-evolution of the Nitrogen and Oxygen Cycles on Earth

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The rise of free oxygen in the Earth's atmosphere, approximately 2300 Ma appears to have been delayed by approximately 400 Myr from the emergence of oxygenic photoautotrophs. One possible constraint of the oxidation process was the interaction of oxygen with other, essential, nutrient elements. We hypothesize that a negative feedback between the nitrogen cycle and oxygen evolution retarded the rate of oxygen production and limited final concentration of oxygen in Earth's Archaean atmosphere. To examine the feedback processes, we developed a coupled biogeochemical model of the oxygen, nitrogen, and carbon cycles and examined how the behavior of these three elements is related to ocean circulation, the relative area of continental shelves, and the initial concentration of phosphate in the ocean. The model results suggest that the nitrogen cycle poses a constraint on the oxidation status of Earth. That constraint continues to the present time.

U52C-02 1615h

The Use of Manipulations in Studies of Nitrogen and Carbon Cycling in Modern Microbial Mats

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Modern microbial mats, laminated microbial communities analogous to the oldest known forms of benthic ecosystems on Earth, contain an invaluable biogeochemical and molecular record of processes and microorganisms thought to be important in their formation over geologic time. We are conducting manipulations of environmental conditions thought to be important in the ecology of microbial mats in order to better understand mat biogeochemical cycling. We present here the results of long-term (ca. one year) manipulations of nutrient and sulfate concentrations in water overlying mats kept in a greenhouse. As the element often limiting production in the marine environments, nitrogen takes on special significance in microbial mat ecology. Microbial mats are often the sites of high rates of N fixation (the energetically expensive conversion of atmospheric dinitrogen into a biologically useful form) and mats host an extremely diverse assemblage of nitrogen fixing microorganisms. Incubation of mats in the absence of nutrient additions resulted in the developments of higher rates of nitrogen

fixation as the community of nitrogen fixing microorganisms responded to the shortage of nitrogen. Additions of phosphorus additionally stimulated nitrogen fixation whereas additions of combined nitrogen suppressed nitrogen fixation. We have also incubated modern microbial mats at the lower sulfate concentrations thought to be present in the Archaean and early Proterozoic Eons. On the modern Earth, high concentrations of sulfate enable sulfate reducing microorganisms to out-compete methanogens for substrates, consequently dominating the degradation of organic carbon in the marine environment. However, very high rates of microbial methane production are implicated in generating the high atmospheric methane concentrations thought necessary to counteract the effects of a less luminous sun during the Archaean and early Proterozoic. Lowered sulfate concentrations in our manipulations did result in lowered rates of sulfate reduction, and an increased (up to six fold higher) flux of methane from these mats. The quantitative importance of methanogenesis in carbon remineralization, even under low sulfate conditions, was, however, relatively small. The results of these experiments demonstrate the utility of environmental manipulations in examining biogeochemical cycling in the environments in which they evolved, namely complex communities of microorganisms.

U52C-03 1630h

Mathematical simulation of the diel O₂, S, and C biogeochemistry of a hypersaline microbial mat

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The creation of a mathematical simulation model of photosynthetic microbial mats is an important step in our understanding of key biogeochemical cycles that may have altered the atmospheres of early Earth and of other terrestrial planets. A modeling investigation is presented here as a tool to utilize and integrate empirical results from research on hypersaline mats from Baja California, Mexico into a computational system that can be used to simulate biospheric inputs of trace gases to the atmosphere. An early version of our model calculates fluxes and cycling of oxygen, sulfide, and dissolved inorganic carbon (DIC) via abiotic components and via the major bacterial guilds: cyanobacteria (CYA), sulfur reducing bacteria (SRB), purple sulfur bacteria (PSB) and colorless sulfur bacteria (CSB). We used generalized monod-type equations that incorporate substrate and energy limits upon maximum rates of metabolic processes such as photosynthesis and sulfate reduction. We ran a simulation using temperature and irradiance inputs from data collected from a microbial mat in Guerrero Negro in Baja Mexico. Model oxygen, sulfide, and DIC results compared well with data collected in the field mats. A divergence from the field data was an initial large negative DIC flux early in the morning and little flux into the mat thereafter in the simulation. We hypothesize that this divergence will be reduced or eliminated if the salinity of the water surrounding the mat were used as an environmental input and as a limit to photosynthesis rates. Salinity levels, organic carbon, methane, methanogens and green non-sulfur bacteria will be added to this model before it is incorporated into a global model to simulate geological time scales.

URL: <http://geo.arc.nasa.gov/sge/casa/>

U52C-04 1645h

Not Just a Poison: Microbes That Derive Energy From Arsenic and Their Linkages to the C, N, and S Cycles.

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Elements that are abundant in the Earth's crust and the microbes that derive energy from them have been the focus of much research in geomicrobiology. However, some trace elements also have significant biogeochemical cycles that are mediated by microorganisms, but the wider implications of these phenomena have generally been overlooked. This has been the case for arsenic. Arsenic is a toxicant owing to its action as an analog of its Group VB neighbor phosphorus. However, a surprising finding was that a wide diversity of anaerobic prokaryotes gain energy for growth by using arsenate as their electron acceptor, and that they are broadly distributed in nature. They carry out the dissimilatory reduction of arsenate to arsenite while oxidizing organic matter (or hydrogen). Since the electrochemical potential of the arsenate/arsenite couple is 60 mV, it acts as an oxidant of more reduced species like sulfide (~ 220 mV). Some arsenate