

## Session 15. The Evolution of the Biogeochemical Cycling of Phosphorus and Other Bioessential Elements

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The origin and evolution of geochemical cycles of bioessential elements is intimately related to the origin and evolution of life on Earth. The biogeochemical cycles of carbon, nitrogen, phosphorus, sulfur and iron were indubitably affected by changes in conditions at the Earth's surface, such as variations in the redox state of the atmosphere and oceans, climate change, and the availability of primary sources of these elements. This session aims to bring together researchers studying the evolution of element cycling from the early Earth to the present day.

We particularly invite abstracts focused on phosphorus, a key element for life which plays a major role in replication, metabolism, and cellular structure. Because of these important functions, phosphorus has been an essential nutrient in biogeochemical cycles since the emergence of life on Earth and its scarcity has imposed limitations on primary productivity. For instance, the evolution of the phosphorous cycle is evidenced by the occurrence of temporally restricted phosphorite deposits in the rock record. However, the evolution of the phosphorus cycle over geological time scales remains poorly understood. A more complete comprehension of the biogeochemical cycle of phosphorus and other interconnected elements will come from studies in cosmochemistry, prebiotic chemistry, oceanography, geology, biochemistry and microbial ecology. Abstract submissions from all these varied perspectives are encouraged.

### 15-01-P. Pyrophosphate and Triphosphate Production Near Hadean Beach Natural Nuclear Reactors

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A Hadean radioactive placer beach would produce hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as a result of radiolysis of water due to fission of fissile and fertile fuels such as Uranium-235, Plutonium-244, and Thorium-232, and due to decay of elements such as Potassium-40. The heaviest placer minerals accumulate near the high-tide mark of beaches due to tidal sorting. A natural nuclear reactor, fueled by fissionable elements within heavy minerals such as uraninite and monazite, would set up a redox gradient as hydrogen gas preferentially escaped, leaving an oxidized core as observed at the Oklo reactor sites in Gabon. H<sub>2</sub>O<sub>2</sub> produced from interstitial water inside the core would migrate to the surrounding area due to nuclear thermal convection and sinusoidal lunar tides. The lunar tide profile also introduces the tantalizing possibility of wetting and drying reactions occurring at the prebiotic site. An experiment was constructed to simulate the mixing of reduced reactants presumably found in the early Earth hydrologic environment (dissolved phosphite and Fe<sup>2+</sup>) with the oxidizing reactants formed within a naturally occurring nuclear reactor (dissolved H<sub>2</sub>O<sub>2</sub>). Orthophosphate (67 percent), pyrophosphate (30 percent), and triphosphate (3 percent) were produced at room temperature upon simple mixing of the reactants. Predictions based on reaction kinetics indicate that, with levels commensurate with H<sub>2</sub>O<sub>2</sub> production from a natural nuclear reactor, the reaction would proceed to completion within 40–60 seconds. Since this completion time is much shorter than the tidal period, the condensed phosphate levels would have reached saturation and crystallized or precipitated near the natural nuclear reactor.

### 15-02-O. Using O-Isotopes to Trace the Evolution of Biogeochemical Cycling of Phosphorus

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The <sup>18</sup>O/<sup>16</sup>O ratio of phosphate ( $\delta^{18}\text{Op}$ ) is a very useful proxy for investigating the biogeochemical cycling of P. On Earth, the dominance of P cycling by biota has resulted in the evolution of  $\delta^{18}\text{Op}$  values away from abiotic source values (*e.g.*, apatite, meteorite-derived phosphite) toward biological endmember values. This is an approx. 20 permil shift in the case of an igneous apatite source and marine phosphate, Earth's largest P reservoir. Recent advances in micro-analytical techniques now allow analysis of  $\delta^{18}\text{Op}$  from a wide range of samples including seawater, DNA, BIF's and meteorites. Despite these advances, impediments to new applications of  $\delta^{18}\text{Op}$  have arisen from the common assumption that phosphate is characterized by only kinetic isotope effects similar to C or N, and the observation that  $\delta^{18}\text{Op}$  is not always a conservative tracer of P sources. The unexpected isotopic behavior of phosphate—dynamic, dominated by equilibrium isotope effects—has, overshadowed potential new applications of  $\delta^{18}\text{Op}$  as a: tracer of biogeochemical P-cycling, recorder of specific microbial metabolisms and phosphoenzyme activities, and as a biomarker—an important application recently bolstered by results of Donald *et al.* (2006) showing that  $\delta^{18}\text{Op}$  values are not reset with increasing metamorphic grade until above 530°C. Guidelines for these and other new applications of  $\delta^{18}\text{Op}$  as well as results of recent studies of reduced-P cycling, will be presented.

### 15-03-O. Recent Advances in the Prebiotic Phosphorylation of Nucleosides and Nucleoside Analogues

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Phosphorylation of nucleosides may have been important during chemical evolution on the early Earth. Potentially prebiotic phosphorylation mechanisms have been demonstrated: drying nucleoside solutions containing urea or formamide over apatite gives high yields of nucleotide isomers, and trimetaphosphate has been shown to be an effective phosphorylating reagent. Phosphorylation reactions were compared to examine their scope. RNA nucleosides, however, may not have been important in the origin of life due to the difficulty of their prebiotic synthesis, thus various analogues were also tested to see whether they were more favorably phosphorylated. Experiments were conducted across a wide range of pH, temperature, and concentration. Nucleoside phosphorylation from drying solutions of urea or formamide was effective if the starting concentrations of reactants were high. Phosphorylation using urea proceeded well at 0.1 M, but did not work when more dilute ( $10^{-2}$  M or lower) solutions were used or below  $\sim 60^{\circ}\text{C}$ . Decomposition of formamide or urea during drying may be partially responsible, as may the high relative humidity of the mixture in the final dry state. The presence of high concentrations of NaCl was not found to inhibit the reaction markedly. Trimetaphosphate was found to be a generally sluggish phosphorylating reagent. The major reaction of the purine nucleosides was depurination. Phosphorylation was generally more efficient at lower temperature with respect to depurination. Acyclic nucleotide analogues were able to be phosphorylated under the same conditions, with markedly less degradation than RNA nucleosides. The implications of these results for the origin of life are discussed.

### 15-04-O. The Marine Phosphorus Cycle in the Archean and Paleoproterozoic

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The availability of phosphate to marine ecosystems in the Archean and Paleoproterozoic was a function of feedbacks involving marine P sources and sinks. The flux of phosphate to the oceans was probably controlled by phosphate release from river-borne reactive particulate phases deposited in continental margin settings, just as it is today. These reactive particulate P phases comprise phosphate that was liberated from rocks during chemical weathering and that subsequently became associated with a labile particulate phase. In the modern ocean, roughly 80–90 percent of phosphate inputs to the oceans are the result of benthic release of particulate phosphorus following early diagenetic alteration of P-labile phases. Estimates for the P weathering flux and the efficiency of diagenetic release of P during the Archean and Paleoproterozoic are quite uncertain. We consider the impact on these phosphate fluxes relative to modern attributable to a primitive terrestrial biosphere and low oxygen atmosphere. Finally, two prominent sinks for marine phosphate in the ancient oceans are evaluated: phosphorites and BIF iron-associated phosphate. Three plausible scenarios emerge, (a) these phosphate sinks, when active, were small relative to other sinks for reactive P in the early oceans; (b) these sinks were significant but of short duration and represent excursions in the marine P cycle; (c) weathering and diagenetic release of weathered P provided substantially less phosphate to the Archean and Paleoproterozoic oceans, hence phosphorites and BIFS represented significant fractions of total P removal at the time of their formation.

### 15-05-O. The Black Sea Nitrogen Cycle: A Glimpse into the Mid-Proterozoic

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The mid-Proterozoic ocean (1.8–1.2 Ga bp) may have resembled the present-day Black Sea with an oxygenated surface layer, a suboxic layer, and a sulfidic deep layer. We study the Black Sea's nitrogen cycle by combining time series of molecular biological and isotope geochemical data to examine the interactions between specific groups of microbes and the chemistry of the Black Sea. There are two potentially competing mechanisms that produce nitrogen gas: heterotrophic denitrification and the anammox process. Denitrification proceeds through an  $\text{N}_2\text{O}(\text{g})$  intermediate while the anammox process does not. Furthermore, denitrification is considered to be a heterotrophic process whereas anammox is potentially autotrophic. Therefore, we hypothesize that pulses of organic matter into the Black Sea (and perhaps the mid-Proterozoic ocean) should favor denitrification and increase atmospheric  $\text{pN}_2\text{O}$ . Our measurements of nitrogen species concentrations and natural stable isotopes show that the  $\text{N}_2$  gas flux out of the suboxic zone is greater than the nitrate and ammonia influx, and molecular data indicate the presence of anammox bacteria at depths where no ammonia is present. Therefore, we propose that nitrogen-rich organic matter stimulates both denitrification and anammox, and the two reactions may co-exist due to vertical spatial separation along the redox gradient. Incubation experiments with isotope tracers are being used to test this hypothesis.

### 15-06-O. The Co-Evolution of Nitrogen and Molybdenum Biogeochemical Cycles: Mo Requirements for Nitrogen Assimilation in Diazotrophic Heterocystous Cyanobacteria

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The geochemical histories of oxygen, nitrogen and molybdenum are intertwined due to the presence of Mo in numerous enzymes involved in the N cycle, and the redox sensitivities of N and Mo. Mo is required for nitrate reductase enzymes that assimilate nitrate in prokaryotes and eukaryotes, as well as the prokaryotic N fixation enzyme nitrogenase. Mo and nitrate were scarce in the ocean before the Great Oxidation Event  $\sim 2.3$  billion years ago. Afterward, nitrate availability increased, but Mo was not abundant until the Neoproterozoic. Therefore, it is important to understand nitrate assimilation when Mo is scarce. We are investigating Mo requirements for nitrate assimilation by a diazotrophic heterocystous cyanobacterium, *Nostoc* sp. PCC 7120, using physiological, genetic and biochemical techniques. When grown on nitrate without added Mo, *Nostoc* sp. PCC 7120 maintains the growth rate and nitrate reductase activity of the replete Mo condition. We hypothesize that these cyanobacteria are adapted to assimilate nitrate at low Mo concentrations. Furthermore, we have identified two previously uncharacterized genes in the *Nostoc* sp. PCC 7120 genome, one of which may encode a Mo storage protein, and the other an alternative nitrate reductase, under low Mo conditions. Characterization of the biochemistry and metal content of these proteins, and the conditions under which they are expressed, is underway. Study of such “fossil” proteins, in addition to other Mo-based N metabolic pathways, suggests that heterocystous cyanobacteria—thought to have been important marine primary producers in the Proterozoic—evolved strategies to cope with low Mo.

### 15-07-P. Evolution of Photosynthesis and Biospheric Oxygenation Are Contingent Upon Nitrogen Fixation?

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How photosynthesis by Precambrian cyanobacteria oxygenated Earth's biosphere remains incompletely understood. Here it is argued that the oxic transition, which took place between approximately 2.3 Gyr and 0.5 Gyr ago, required a great proliferation of cyanobacteria, and this in turn depended on their ability to fix nitrogen via the nitrogenase enzyme system. However, the ability to fix nitrogen was not a panacea, and the rate of biospheric oxygenation may still have been affected by nitrogen constraints on cyanobacterial expansion. Evidence is presented for why cyanobacteria probably have a greater need for fixed nitrogen than other prokaryotes, underscoring the importance of their ability to fix nitrogen. The connection between nitrogen fixation and the evolution of photosynthesis is demonstrated by the similarities between nitrogenase and enzymes critical for the biosynthesis of (bacterio)chlorophyll. It is hypothesized that biospheric oxygenation would not have occurred if the emergence of cyanobacteria had not been preceded by the evolution of nitrogen fixation, and if these organisms had not also acquired the ability to fix nitrogen at the beginning of or very early in their history. The evolution of nitrogen fixation also appears to have been a precondition for the evolution of (bacterio)chlorophyll-based photosynthesis. Given that some form of chlorophyll is obligatory for true photosynthesis, and its light absorption and chemical properties make it a 'universal pigment,' it may be predicted that the evolution of nitrogen fixation and photosynthesis are also closely linked on other Earth-like planets.

### 15-08-P. Nitrogen Cycling in a Novel Symbiosis: An Examination of Nitrogen Fixation by an Endosymbiont in a Marine Shipworm

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A critical component of the global nitrogen (N) biogeochemical cycle is biological nitrogen fixation, the metabolic process used by many Bacteria and Archaea to generate new biologically available N from inert atmospheric N<sub>2</sub>. Biological nitrogen fixation may have been essential to the evolution of all life on Earth because of its close link with the evolution of photosynthesis (Grula, *Int J Astrobiology* 4, 2005). Many present-day organisms and ecosystems in N-limited conditions are dependent upon nitrogen fixation for fixed N. One such example of an organism is the marine wood-boring bivalve (shipworm), *Lyrodus pedicellatus*. It has a wood-based (cellulose-rich, N-poor) diet, and the shipworm hosts multiple bacterial endosymbionts within gill bacteriocytes that assist it with cellulose digestion and with N supplementation to the diet. *In situ* nitrogen fixation has been demonstrated using intact shipworms, and newly fixed N is transferred to symbiont-free host cells. We utilized the sole cultured endosymbiont *Teredinibacter turnerae* to investigate some of the critical parameters that make this symbiosis viable and control the activity of the symbiosis. First, we explored the potential effects of ammonium, which may be present in host tissue, on symbiont nitrogen fixation. Second, we explored the mechanisms through which endosymbionts may translocate newly fixed N products to the host. Nutrient analysis on culture filtrate indicates that *T. turnerae* does not excrete significant quantities of dissolved inorganic nitrogen in the form of ammonium or nitrate.

### 15-09-O. Fractionation of Oxygen Isotopes in Phosphate During Phosphate-Iron Oxide Interactions

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Iron oxides play an important role in the biogeochemical cycling of phosphorus. We have studied oxygen-isotope fractionations during the sorption of dissolved inorganic orthophosphate to iron oxides in abiotic systems. The sorption of phosphate onto synthetic ferrihydrite was performed at pH 8.2 in artificial sea water media at different temperatures ranging from 4 to 95°C mimicking conditions relevant to deep-sea hydrothermal vents. The speciation of phosphate into sorbed and solution phases was quantified and the oxygen isotope ratio of phosphate was measured. Similarly the transformation of ferrihydrite to goethite was measured by X-ray diffraction and Raman spectroscopy. Our results show that the uptake of phosphate by ferrihydrite was fast with 50 percent of phosphate sorbed within 5 minutes, and the rate of uptake at high temperature was slightly faster than that at low temperature. The oxygen isotope fractionation during this speciation varied from 1.7 to 4.2 permil at 4 and 95°C, respectively at early stages of the experiments. This fractionation gradually decreased and became almost zero for any time more than 500 hours. Although some phosphate desorbed during the transformation of ferrihydrite to goethite at high temperature, isotopic fractionation due to this process was not detected. These results suggest that the fractionation of oxygen isotopes in phosphate is kinetic and is prevalent only at early stages of reaction/speciation with no fractionation detected at long reaction times.

### 15-10-P. Compound Specific Nitrogen Isotopes Utilizing Multiple Geoporphyrins and Chlorines During Cretaceous Oceanic Anoxic Events: Understanding the Impact of Redox Changes on the Nitrogen Cycle

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Compound specific nitrogen isotope analyses on geoporphyrins and chlorines have unique potential in that they can link nitrogen isotope values directly to chlorophyll and primary producers. Nitrogen isotope values from bulk sediments have proven useful for numerous recent studies investigating the state of the nitrogen cycle in the past, however questions remain as to the fidelity of such records. It is therefore advantageous to utilize compound specific methods. We focus on Oceanic Anoxic Event 2 from the mid-Cretaceous as an analogue for large-scale marine redox changes through time. Nitrogen isotope records of bulk sediments from OAE 2 have values that are typically less than 0 permil and in some cases show a 2–3 permil negative excursion through the OAE. These values are interpreted to be the result of primary producers utilizing nitrogen substrates produced by nitrogen fixers and the variability reflects chemocline rise and its impact on nutrient cycling through the OAE. Nitrogen isotope data from geoporphyrins and chlorins from OAE 2 sediments allow us to assess this hypothesis. Initial compound specific nitrogen isotope data through OAE 2 reflect the negative excursion in bulk N-isotopic values, however, the range of values is greatly expanded and the negative excursion is as large as 10 permil. These data support earlier hypotheses suggesting large changes in oceanic nitrogen cycling during OAE 2 however the large range and anomalously positive N-isotopic values outside of the OAE suggest that we may have greatly underestimated the change in nitrogen cycling during OAE II.

## 15-11-O. Phosphorus Redox Chemistry Within Planetary Environments

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On Earth, phosphorus occurs naturally as fully oxidized orthophosphate ( $\text{PO}_4^{3-}$ ) most commonly within igneous and metamorphic rocks as the apatite family  $\text{Ca}_5(\text{PO}_4)_3(\text{X})$  [ $\text{X} = \text{Cl}, \text{F}, \text{OH}$ ]. However, the low solubility of orthophosphate salts in water coupled with low inherent chemical reactivity has raised doubts as to whether orthophosphates were Nature's first choice P-chemical en route to life on Earth. Alternatives to orthophosphates have been suggested<sup>3</sup> but concrete evidence for any of these species on the prebiotic Earth has yet to be provided. However, Gulick's proposal<sup>1</sup> that the lower oxidation state phosphorus oxyacids H-phosphonic ( $\text{H}_3\text{PO}_3$ ) and H-phosphinic ( $\text{H}_3\text{PO}_2$ ) could have been more effective phosphorylating agents than orthophosphate has been given a boost by recent discoveries by Pasek & Lauretta in Arizona<sup>2</sup> and in our own laboratory.<sup>3</sup> These studies revealed that schreibersite inclusions,  $(\text{Fe}, \text{Ni})_3\text{P}$ , within iron meteorites undergo anaerobic redox transformations in water to afford principally H-phosphonic acid under thermal and H-phosphinic acid under photochemical conditions. Here we describe the production of phosphorus species in five different oxidation states resulting from the hydrolytic modification of schreibersite inclusions under a variety of conditions including UV and microwave induced plasma irradiation. In addition we discuss how such reduced oxidation state P-species may have impacted upon an early Earth biosphere and further report the first application of scanning vibrating electrode technique (SVET) and scanning Kelvin probe (SKP) analyses to probe corrosion of meteorite surfaces.

1. A. Gulick, A., 1955. *Am. Scient.*, 43:479.

2. Pasek, M.A., Lauretta, D.S., 2005. *Astrobiology*, 5:515.

3. Bryant, D.E., Kee, T.P., 2006. *Chem. Commun.*, 2344.

## 15-12-O. Was There Really an Archean Ocean Phosphate Crisis?

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During the Archean, massive amounts of iron were deposited in the form of banded iron formations (BIF). It has been suggested that during BIF deposition, sedimenting particles of ferric oxyhydroxide may have stripped dissolved phosphate from the ocean's photic zone; based on BIF P-content, phosphate concentrations of only 10–25 percent of present-day values have been suggested. Such low P concentrations would have led to a reduction in phytoplankton productivity, and therefore, to lower rates of oxygen production and organic carbon burial. This model is predicated on the observation that ferric oxyhydroxide particles, resulting from the oxidation of Fe(II) in some modern submarine hydrothermal systems, sequester phosphate with a  $K_d$  value of approximately  $0.06 \mu\text{M}^{-1}$ . However, this model did not take into account the high concentration of dissolved silica that was present in seawater at that time, which was at least as high as at saturation with cristobalite, and possibly even amorphous silica. We show experimentally that silica effectively competes with phosphate for available sorption sites on ferrihydrite particles. Furthermore, co-precipitation of silica with ferrihydrite reduces the resulting particle's reactivity towards phosphate. Our results demonstrate that silica-containing ferrihydrite particles sequester phosphate much less strongly than silica-free ferrihydrite particles, and in light of BIF P-content, indicate that Archean oceans likely contained significantly more phosphate than previously believed. Thus, it is unlikely that there was a phosphate crisis in the Archean ocean due to BIF deposition.

## 15-13-P. Tracking the Rise of Atmospheric Oxygen and Related Environmental Changes During the Paleoproterozoic: 3.6 km of Drillcores from 2.5–2.0 Ga Rocks from Russian Fennoscandia

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The Paleoproterozoic is one of the critical time intervals in the evolution of the Earth System when biota, atmosphere, hydrosphere and geosphere experienced global-scale changes. Widespread rifting activity, possible upper mantle oxidation, the global Huronian glaciation(s), a rise in atmospheric oxygen, the Lomagundi-Jatuli carbon isotope excursion, an increase of oceanic sulfate, formation of oldest known phosphorites, change in organic matter mineralization and generation of significant amounts of petroleum are among hallmark events/processes that characterize this time interval.

The Fennoscandian Arctic Russia–Drilling Early Earth Project (FAR-DEEP) has been established in the framework of the International Continental Drilling Program (ICDP) to study these events and processes in sedimentary and volcanic successions of the Onega basin and Pechenga and Imandra-Varzuga greenstone belts. It is expected that the cores from 15 holes totaling 3560 m that were obtained from Onega, Pechenga, and Imandra-Varzuga during the drilling campaign in May–October 2007 will provide a unique rock archive for the period 2.5–2.0 Ga. The cores will be archived at the Geological Survey of Norway in Trondheim, and will be available for sampling and research by the international group of FAR-DEEP scientists in fall 2008. The entire science community will have access to the cores after a one-year moratorium period. The FAR-DEEP scientists cover a wide range of expertise and research objectives. However, the project is still open for new associates in the research fields that are essential for tracking the environmental upheavals during the Paleoproterozoic. For additional information refer to <http://far-deep.icdp-online.org>

## 15-14-P. The Use of Molecular Techniques to Explore Nitrogen Fixation and Utilization Among Freshwater Phytoplankton

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Nitrogen is a bioessential and often limiting nutrient in aquatic ecosystems. As such, nitrogen availability is capable of influencing the closely linked and globally important process of carbon uptake by phytoplankton. We describe the use of molecular techniques to identify changes in nitrogen fixation and nitrogen utilization as phytoplankton communities change during the process of seasonal succession. To determine the year-round potential for nitrogen fixation in one temperate lake, total DNA was extracted from biweekly phytoplankton samples taken from Lake Pueblo, in Pueblo, Colorado. Prokaryotic nitrogen fixation is then assessed through the amplification of highly conserved regions of the nitrogenase enzyme using the polymerase chain reaction (PCR), while nitrogen utilization is assessed through the amplification of highly conserved regions of the nitrogen reductase enzyme. The TOPO cloning technique is then used to clone PCR products into plasmid vectors using topoisomerase I. Plasmids are subsequently transformed into competent bacterial cells, thus amplifying small DNA fragments such that they can be sequenced. This assists in the identification of the species potentially involved in each of these two biogeochemical processes at the specific time periods analyzed. We hope to identify key players in the nitrogen cycle of Lake Pueblo, and to discover symbiotic relationships that may evolve in response to seasonal changes in nitrogen availability. This research represents a collaborative effort between Colorado State University – Pueblo and the University of California Los Angeles supported by the 2007 NAI-MIRS Summer Sabbatical Program.

### 15-15-P. Evaluation of Biological and Enzymatic Activity of Soil in Tropical Dry Forest – Desierto de la Tatacoa (Colombia) with Potential Application in Mars Terraforming and Similar Planets

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Desierto de la Tatacoa has a tropical dry forest bioma. It has a hot thermal floor at an altitude of 440 m; with a daily average temperature of 28°C, and a maximum of 40°C. Its annual rainfall total can be upwards of 1250 mm, its daily average solar sheen is 5.8 hours and its relative humidity is between 65 and 65 per cent. Therefore, the life forms presents are very scant, and in certain places, almost void. We took a random sampling of soil from the surface down to 6 inches, of zones without vegetation and with soils highly loaded by iron oxides in order to determine the number and identity of microorganisms. We also measured the soil basal respiration and determined enzymatic activity (catalase, dehydrogenase, phosphatase, and urease). From our results, we develop an alternative in the study of soil genesis in Mars in particular, and recommendations for the same process on other planets. Although martian soil demonstrates no enzymatic activity, our results propose an alternative to problems like carbonic fixing of the dense martian atmosphere of CO<sub>2</sub> by martian soil, and to the degradation of inorganic compounds in preparation of the substratum for later colonization by life.

### 15-16-O. Identifying Biogeochemical Phosphorus Redox Pathways

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Phosphorus is a key nutrient for life and plays a significant role in several biochemical processes. Up to 20 percent of organic phosphorus in sediments and up to 5 percent in soils actually occurs in organophosphate compounds which have carbon-phosphorus direct bonds. These compounds may be viewed as having a reduced oxidation state (+3) for phosphorus relative to organophosphates, with a P oxidation state of 5+. The biochemistry of phosphonates is poorly understood but may suggest a phosphorus redox biogeochemical cycle. Phosphorus redox pathways are ubiquitous and ancient in microbial lineages (White and Metcalf 2007), suggesting that utilization of reduced phosphorus on the early Earth may have been an evolutionarily preferred trait. Here I will discuss inorganic pathways for phosphorus reduction on the early Earth, and the relative importance of each inorganic reduction pathway. Reduced phosphorus compounds have been discovered in meteorites and other extraterrestrial material, in impactites, in fulgurites (Essene and Fisher 1986), and in some rare volcanic rocks. The formation pathway of reduced P is unclear, but for fulgurites, volcanic rocks, and some impactites, seems intimately linked with the presence of carbon. Of these, extraterrestrial material and impactites appear most relevant to the redox chemistry of phosphorus on the early Earth. *References:* (1) Essene, E.J., Fisher, D.C., 1986. *Science* 234:189–193. (2) White, A.K., Metcalf, W.W., 2007. *Annu. Rev. Microbiol.* 61:379–400.

### 15-17-P. Evidences Support an Extraordinary Event, Possibly an Impact During the Proterozoic for Phosphorus Abundance on the Earth

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The stromatolites of Precambrian Aravalli Supergroup outcropping around Udaipur, Rajasthan, India investigated by Sisodia and Chauhan (1990) have been classified as two distinct lithofacies: carbonate stromatolite facies and phosphate bearing stromatolite facies. There is a sharp and abrupt contact between these two facies, which is of considerable importance as it marks a diastem (small unconformity) characterizing a period of overall change in the environment. The Earth has been subjected to several catastrophic episodes caused by extraordinary high energy events; such as impacts by extraterrestrial bodies which

caused mass extinctions or sometimes emergence of new species. Fossil cyanobacteria of 20 to 100 micrometer diameter, elliptical to circular in shape, occurring singly or in massed colonies have been found in these phosphate-bearing stromatolites. These cyanobacteria accumulated abnormal amount of phosphorus and formed a workable deposit of phosphorite owing to their post-mortem alteration (Sisodia, 1991). The point of discussion is: why phosphorus shows sudden abundance in the milieu which otherwise is absent in the immediately underlying carbonate stromatolites? Bushinski (1969) postulated “upwelling” events for the abundance of phosphorus at some time-units in the Phanerozoic. However during the Precambrian era there was an insufficient amount of dead life sinking to the bottom of the oceans to release phosphorus to upwell later. It can be argued that the sharp boundary (diastem) between the two types of stromatolites noted at Udaipur expresses a possibility of an extraordinary event, possibly an impact that inundated the Earth with phosphorus.

### 15-18-O. Abiotic Nitrogen Reduction in Hadean Hydrothermal Systems

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One of the outstanding questions in Astrobiology is the source and formation mechanisms of NH<sub>4</sub><sup>+</sup> which presumably was required for reactions of prebiotic synthesis and origin of life. The uncatalyzed reduction of abundant dinitrogen (N<sub>2</sub>) to ammonia/ammonium (NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>) is prohibitively slow due to the strong triple bond in the molecule. However, nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) present in the Hadean Ocean as result of atmospheric reactions may have been more susceptible to reduction. We have experimentally tested the hypothesis, which suggests that Ni, Fe metals and their alloys formed as a result of hydrothermal serpentinization processes in the Hadean oceanic crust could have acted as catalysts and/or reactants in reactions leading to abiotic NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>. Our results show NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> were converted into NH<sub>4</sub><sup>+</sup> more rapidly than N<sub>2</sub>, and the reduction process exhibited strong temperature dependence. Metals, especially Ni were found to be more effective than alloys in reducing N<sub>2</sub> with yields usually not exceeding few percent. Based on the experimental results we have estimated NH<sub>4</sub><sup>+</sup> yield of Hadean hydrothermal systems from to be approximately 10<sup>10</sup>–10<sup>12</sup> mol.yr<sup>-1</sup>. Our estimate only includes N<sub>2</sub> to NH<sub>4</sub><sup>+</sup> reaction yield and therefore if NO<sub>2</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> were present in the advected seawater, the yields would have been proportionally higher considering their high conversion rates to NH<sub>4</sub><sup>+</sup> in the presence of metals/alloys. We conclude that reduction of N<sub>2</sub> in serpentinization-driven submarine hydrothermal systems was a viable source of abiotic NH<sub>4</sub><sup>+</sup> on the Hadean Earth.

### 15-19-P. Did Nature Also Choose Arsenic?

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All known life requires phosphorus (P) in the form of inorganic phosphate (PO<sub>4</sub><sup>-</sup> or Pi) and phosphate-containing organic molecules. Pi serves as the backbone of the nucleic acids that constitute genetic material and as the major repository of chemical energy for metabolism in polyphosphate bonds. Arsenic (As) lies directly below P on the periodic table and so the two elements share many chemical properties. Although their chemistries are sufficiently dissimilar that As cannot directly replace P in modern biochemistry, As is toxic precisely because these elements are similar enough that organisms attempt this substitution. We hypothesize that ancient biochemical systems, analogous to but distinct from those known today, could have utilized arsenate in the equivalent biological role of phosphate. Such ‘shadow life’ could have existed at the time of the origin and early evolution of life on Earth or on other planets. It may even persist, undetected, in unusual niches today.

## 15-20-O. Chemical Weathering and Gas Transfers During Microbial Acquisition of P from Basalt

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We used batch reactors to quantify chemical weathering phenomena and associated gas transfers ( $O_2$  and  $CO_2$ ) during interaction of a single heterotrophic bacterial species (*Burkholderia fungorum*) with basalt at  $T = 28^\circ C$  for 36 days. We supplied glucose and  $NH_4^+$  as C and N sources, respectively, and trace apatite in basalt as a P source. The goal was to evaluate how bacteria might influence the chemical evolution of Earth's hydrosphere and atmosphere by coupling the C, N, and P cycles at the water-rock interface. Cell numbers increased  $\sim 3$  orders of magnitude, demonstrating that *B. fungorum* used apatite-bound P for biomass synthesis. Microbially-mediated Ca, Mg, and Si release rates from basalt were 2.66, 1.09, and  $1.72 \times 10^{-12}$  mol/m<sup>2</sup>/s, respectively. The P release rate was  $0.24 \times 10^{-12}$  mol/m<sup>2</sup>/s, but bacteria scavenged all dissolved P. Abiotic control reactors yielded much lower release rates. Rapid elemental release in biotic reactors resulted from pH lowering, in particular gluconic acid release and  $H^+$  extrusion during  $NH_4^+$  uptake. The transfer of P from apatite to bacteria during C and N utilization yielded an  $O_2$  consumption rate of  $7.06 \times 10^{-12}$  mol/m<sup>2</sup>/s and a  $CO_2$  release rate of  $8.40 \times 10^{-12}$  mol/m<sup>2</sup>/s. When viewed in the context of the long-term carbon cycle, heterotrophic bacteria utilizing glucose and  $NH_4^+$  appear to elevate the rate of atmospheric  $CO_2$  consumption by Ca-Mg silicate weathering to  $3.75 \times 10^{-12}$  mol/m<sup>2</sup>/s, which is a factor of  $\sim 5$  higher than the corresponding inorganic rate.

## 15-21-O. Phosphorus Chemistry in the Interstellar Medium: From Circumstellar Shells to Meteorites?

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Phosphorus plays an important role in biological systems, being a key element in DNA, RNA, and ATP. Its prevalence in living systems is in fact far enhanced over its natural cosmic abundance. This result has led to the suggestion that the phosphorus that became incorporated into living systems was brought to Earth in concentrated form via schreibersite, (Fe, Ni)<sub>3</sub>P, in meteorites. Where did schreibersite originate? Thermochemical calculations suggest that schreibersite is the main phosphorus condensate in both oxygen- and carbon-rich circumstellar envelopes of evolved stars. Can this mineral be traced back to circumstellar environments? Observations of gas-phase phosphorus-bearing molecules suggest that the chemistry of this element is quite active in circumstellar gas. CP, PN, and HCP have been detected in carbon-rich envelopes (see Milam *et al.* 2008), and recently PO and PN have been detected in the oxygen-rich shell of the supergiant star VY Canis Majoris (Ziurys *et al.* 2007; Tenenbaum *et al.* 2007). Very recently, CCP has been detected in the carbon-rich shell of the star IRC+10216 (Halfen *et al.* 2008). In contrast, the only phosphorus-bearing species observed in molecular clouds thus far is PN. Thus, condensation onto grains, perhaps into schreibersite, may be removing phosphorus from the gas phase in circumstellar material, and locking it into the solid phase. These current results and their implications for prebiotic chemistry of phosphorus in the interstellar medium will be presented.