Dating the Origin of Life: Present-Day Molecules and First Fossil Record

Symposium

Göttingen Academy of Sciences and Humanities
and Courant Research Centre Geobiology

October, 16-18, 2014

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Joachim Reitner, Hans-Joachim Fritz & Jan-Peter Duda

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Address of Executive Editor:

Professor Dr. Joachim **Reitner**

Georg-August-Universität Göttingen
Geoscience Museum / Department of Geobiology
Goldschmidtstr. 1-5, D-37077 Göttingen, Germany
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E-mail: jreitne@gwdg.de

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The symposium
Dating the Origin of Life: Present-Day Molecules and First Fossil Record
is dedicated to attempts of dating early life processes using molecular clocks, early Precambrian records of biosignatures and biomarkers, and bona fide microbial fossils. It brings together scientists from a variety of disciplines such as geobiology, molecular biology, biogeochemistry and others in order to discuss controversial concepts of the origin of life and the formation of a habitable world in the Archean and early Proterozoic. Ideally, the symposium will create new ideas of how to link known sequences of early evolutionary events to likewise known markers on an absolute scale of geological time.

The principle of gradual chance of characters is one of the major concepts of evolutionary theory. Comparison of characters, morphological or molecular in nature, allows the reconstruction of phylogenetic trees. These, however, while delineating the relative sequence of branching of new taxa, do not as such address the question of absolute time intervals between branch points. For this it is necessary to correlate branching knots with the occurrence of certain fossils of known absolute age (i.e. determined by geological methods such as radiometric isotope clocks). Complementary methods of deriving time information from sequence distances of biological macromolecules date back to the early 1960ies when Pauling and Zuckerkandl introduced the concept of "Molecular Clocks".
Modern genome analysis, however, revealed that in second approximation this concept is fraught with a number of difficulties stemming from lateral gene transfer (LGT), mutation rates varying with time etc. In order to fully exploit the potential of the vast amount of genomic data available, molecular clocks will have to be more closely calibrated against geological clocks and a history of LGT and of mutation rates to be determined on a wide scale. Until then, reconstruction of a time-scaled tree of life in geologically old periods (Precambrian) will remain a difficult and contentious issue.

The early geological record of Earth during its first 500 Ma (Hadean) is very poor; only some minerals are known giving us only sparse information of early Earth processes. Due to heavy impacts of large cosmic boulders (asteroids, meteorites, comets) and heavy volcanic eruptions, the upper surface of the Earth was often destroyed with the effect of resetting radiometric clocks. However, a first window for the shift from organic geochemistry to cellular life may have opened in the last part of the Hadean (4.2-4.0 Ga). An alternative is offered by of "Panspermia" (an idea promoted, among others, by Crick and Orgel since the 1970ies). According to this concept, comets and meteorites could have served as vehicles to transport life from other cosmic sites to Earth. While undoubtedly simple organic matter has been brought to Earth aboard impactors, there is no evidence to date that intact informational macromolecules, let alone complex cellular life, ever arrived by this mechanism. Either way, early life would have benefited by the end of the so-called Heavy Bombardment (around 3.9 Ga) and the stabilization of ecological conditions in the subsequent Archean.

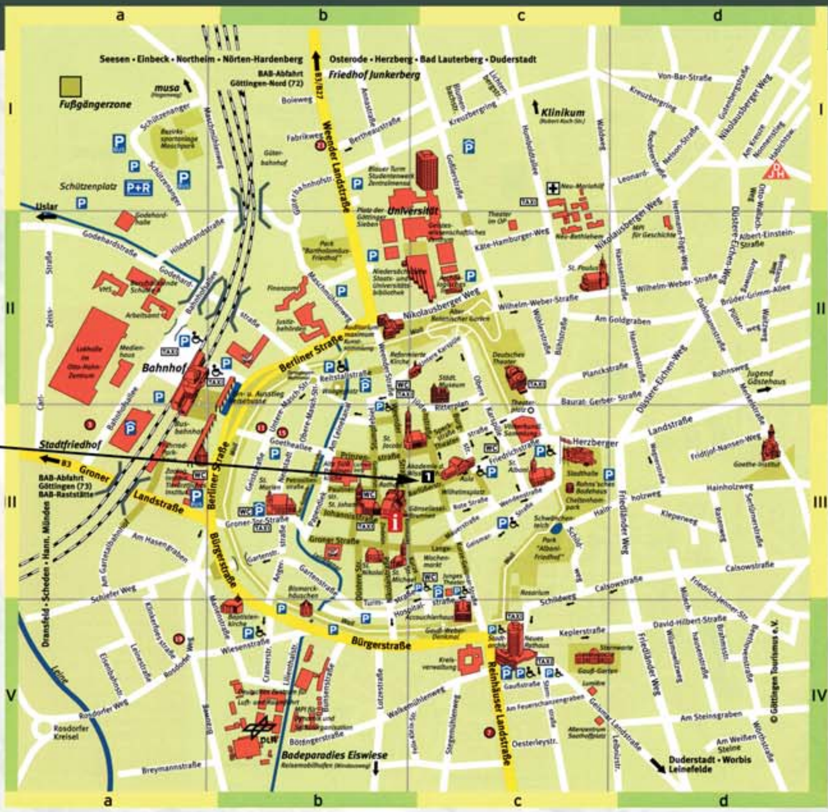
Professor Dr. Joachim Reitner

Professor Dr. Hans-Joachim Fritz

DFG Deutsche Forschungsgemeinschaft

GEORG-AUGUST-UNIVERSITÄT GÖTTINGEN

CRC Courant Research Centre Geobiology



1
Fußgängerzone
Seesen • Einbeck • Northeim • Nörten-Hardenberg
Osterode • Herzberg • Bad Lauterberg • Duderstadt
Friedhof Junkerberg
Klinikum
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Bahnhof
Stadtfriedhof
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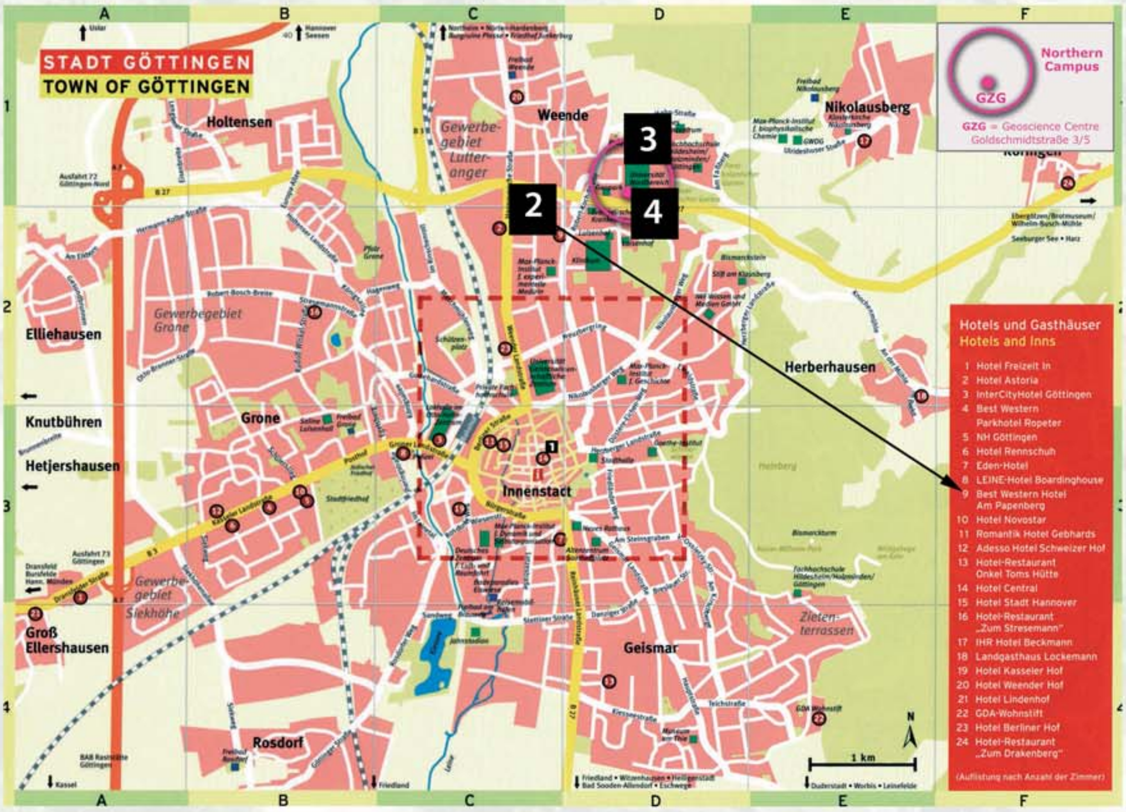

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2
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GZG = Geoscience Centre Goldschmidtstraße 3/5
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Hetjershausen
Grone
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Rosdorf
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2 Hotel Astoria
3 InterCityHotel Göttingen
4 Best Western Parkhotel Ropeter
5 NH Göttingen
6 Hotel Rennschuh
7 Eden-Hotel
8 LEINE-Hotel Boardinghouse
9 Best Western Hotel Am Papenberg
10 Hotel Novostar
11 Romantik Hotel Gebhards
12 Adesso Hotel Schweizer Hof
13 Hotel-Restaurant Onkel Toms Hütte
14 Hotel Central
15 Hotel Stadt Hannover
16 Hotel-Restaurant „Zum Stresemann“
17 IHR Hotel Beckmann
18 Landgasthaus Lockemann
19 Hotel Kasseler Hof
20 Hotel Weender Hof
21 Hotel Lindenhof
22 GDA-Wohnstift
23 Hotel Berliner Hof
24 Hotel-Restaurant „Zum Drakenberg“
(Auflistung nach Anzahl der Zimmer)

1 Göttingen Academy of Sciences and Humanities
Theaterstraße 7
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2 Best Western Hotel Am Papenberg
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3 Max Planck Institute for Solar System Research
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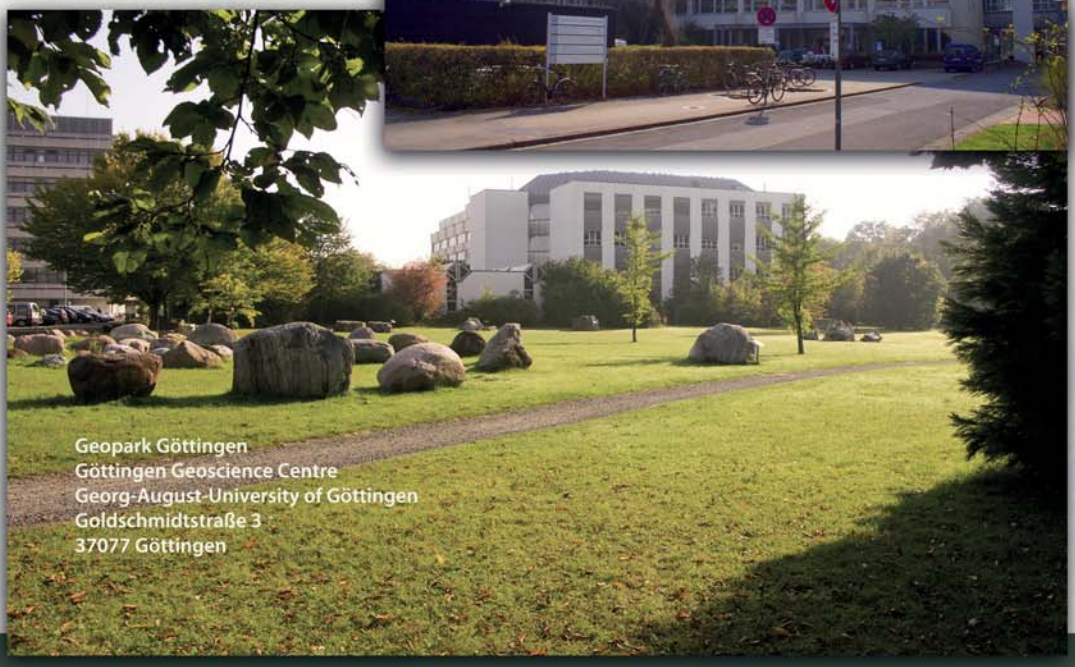


Geopark Göttingen
Göttingen Geoscience Centre
Georg-August-University of Göttingen
Goldschmidtstraße 3
37077 Göttingen

Thursday
16.10. 2014

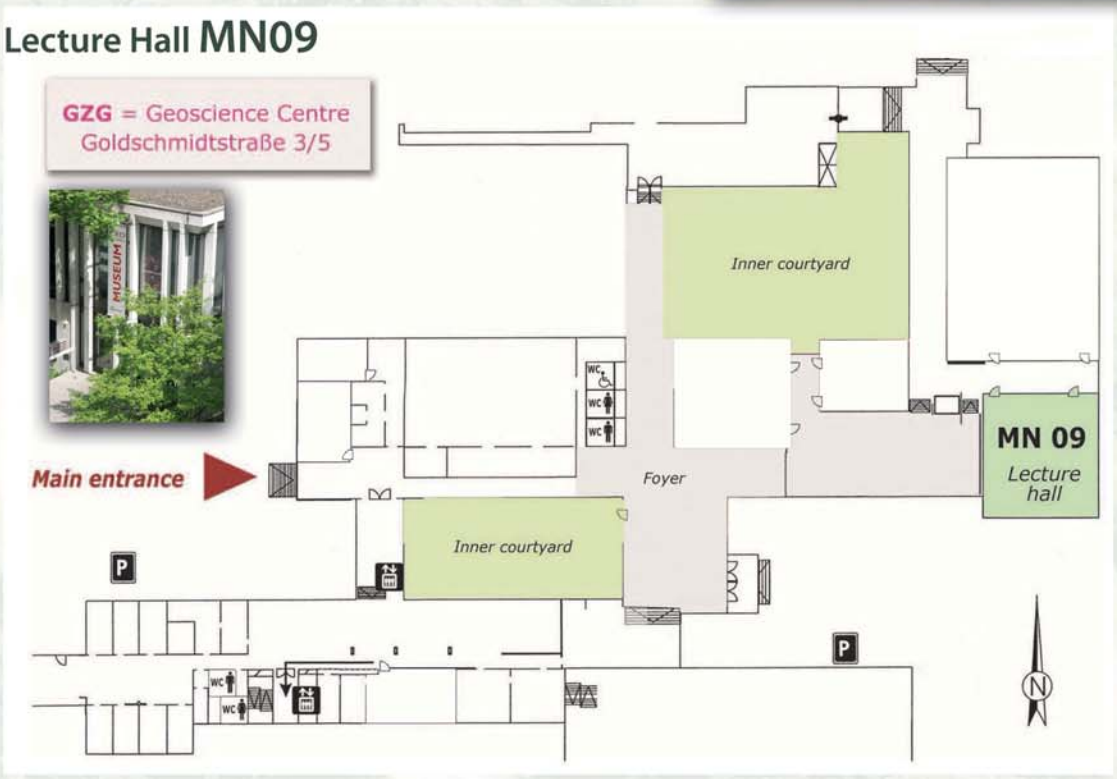
18:30 Ice Breaker

Location:
Göttingen Academy of Sciences and Humanities
Theaterstraße 7
37073 Göttingen

Friday
17.10. 2014

Conference venue:
Göttingen Geoscience Centre
Georg-August-University of Göttingen
Goldschmidtstraße 3
37077 Göttingen

Lecture Hall MN09



Friday
17.10. 2014

Contributions: *Göttingen Geoscience Centre, Georg-August-University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen*

Lecture Hall MN09

8:30 Introduction: *Prof. Dr. J. Reitner & Prof. Dr. H.-J. Fritz*

Welcome Addresses:

Prof. Dr. Stefan Tangermann, President of Göttingen Academy of Sciences and Humanities
Prof. Dr. Sharon Webb, "Dean of the Faculty of Geoscience and Geography, Georg-August-University of Göttingen"

Talks:

1. *9:00 Martin J. Van Kranendonk*
   A Planetary driver of environmental, atmospheric and biological change through the Precambrian
2. *9:30 Chaitanya Giri*
   The organic payload of comets and a scenario for the Late Heavy Bombardment phase
3. *10:00 Andrew Steele*
   What do prions, viruses and viroids reveal about the formation of life on Earth?

Coffee Break: 15 min

4. *10:45 Steven A. Benner*
   The history of life on Earth. Combining the molecular and geological records using experimental paleogenetics
5. *11:15 Blair Hedges*
   Dating the origin of life with molecular clocks and other evidence
6. *11:45 Manolo Gouy, Mathieu Groussina & Bastien Boussaua*
   Molecular thermometers: using ancestral sequence reconstruction to infer the history of adaptation to environmental temperature along the tree of life
7. *12:15 Wilfried Kramer & Hans-Joachim Fritz*
   From RNA to DNA as the genetic storage medium – the history of a stepwise takeover

12:45 – 14:00 Lunch Break

8. *14:00 Bettina E. Schirrmeister*
   The evolution of prokaryotic multicellularity and the oxygenation of Earth
9. *14:30 Andreas Kappler & Kurt Konhauser*
   The role of microbial iron oxidation and iron reduction in deposition and transformation of Precambrian Banded Iron Formations
10. *15:00 Elizabeth D. Swanner and Andreas Kappler*
    The role of Fe in modulating Earth's oxygenation

15:30 Coffee Break 15 Min

11. *15:45 Maximilian Halama, Elizabeth Swanner & Andreas Kappler*
    Simulating diagenesis of Precambrian banded iron formations: The fate of primary iron minerals and organic carbon
12. *16:15 Aude Picard, Andreas Kappler, Gregor Schmid, Luca Quaroni & Martin Obst*
    Experimental diagenesis of modern Fe(II)-oxidizing bacteria to help understanding the fossil record

19:00 Conference Dinner
Restaurant Kalimera, Knochenmühle 1, 37075 Göttingen

A free bus shuttle will be provided during the symposium.

Saturday
18.10. 2014

Contributions: *Göttingen Geoscience Centre, Georg-August-University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen*

Lecture Hall MN09

13. *9:00 Sukanya Sengupta, Andreas Pack, François Robert, Joachim Reitner, Zachary Sharp & Daniel Herwartz*
New approach towards determining temperature isotopic composition of ancient oceans using high precision $\delta^{17}O$ and $\delta^{18}O$ analysis of cherts

14. *9:30 Tom McCollom*
Abiotic pathways for the formation of reduced carbon on the early Earth

15. *10:00 Christian Hallmann*
Steroid biomarkers throughout the Precambrian yield a fresh look on eukaryotic evolution

16. *10:30 Jan-Peter Duda, Joachim Reitner, Martin Blumenberg, Danny Ionescu, Nadine Schäfer, Volker Thiel & Martin Van Kranendonk*
Biogeochemical characterization of Paleoarchaean Rocks from the Pilbara Craton (Western Australia)

Coffee Break: 15 min

17. *11:15 Joachim Reitner, Jan-Peter Duda, Nadine Schäfer, Martin Van Kranendonk, Michael Hoppert, Franziska Wilsky & Bent Hansen*
Early Archean carbonates on early Earth - microbial biosignature versus hydrothermal origin

18. *11:45 Michael Hoppert, Dominik Mühlen & Joachim Reitner*
Biomineral formation by a thermophilic Archaeon as a model for processes in Archean cherts

12:15-13:30 Lunch break

13:30 - 14:30 Bridging the gap: General discussion

15:00 -17:00 Guided Visits: (i) Max-Planck-Institute for Solar System Research, (ii) Museum and Collection of the Department of Geosciences and Geography (University of Göttingen)

Informal farewell get-together: Beer and snacks

A free bus shuttle will be provided during the symposium.

The history of life on Earth. Combining the molecular and geological records using experimental paleogenetics

Steven A. Benner

Foundation for Applied Molecular Evolution, Gainesville, USA; E-Mail: sbenner@ffame.org

In a hypothetical future when all of the species on Earth have at least one representative in the genome sequence database, the history of life on Earth will be represented by a precomputed database of trees that summarize nearest neighbor relationships of the aligned sequences; these will be based on multiple sequence alignments of those sequences, which are hypotheses for the homology relationships of individual nucleotides. Each node in those trees will then be associated with a probabilistic ancestral sequence that is inferred by comparing the descendent sequences using models for nucleotide and amino acid replacements. That record will be necessarily incomplete, due to extinctions, rapid sequence divergence, and imperfect models. The geological record for Earth will similarly be incomplete, due to record loss, metamorphosis, and imperfect models for the accretion and development of the planet. This talk will discuss how these two records can be combined more productively if synthetic biological methods are used to resurrect ancient genes and proteins for studying the laboratory. We will consider in particular the emergence of alcohol formation and consumption, the adaptation to large-scale climate changes, and early events in the origin of translation.

Stromatolites in the 3.35 Ga Strelley Pool Formation (Western Australia).

Biogeochemical characterization of Paleoarchean Rocks from the Pilbara Craton (Western Australia)

Jan-Peter Duda[1], Joachim Reitner[1], Martin Blumenberg[1,2], Danny Ionescu[3,4], Nadine Schäfer[1], Volker Thiel[1] & Martin Van Kranendonk[5]

[1]*Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany; E-mail: jduda@gwdg.de*
[2]*Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany*
[3]*Leibniz Institute for Freshwater Ecology and Inland Fisheries, Department of Experimental Limnology, Stechlin, Germany*
[4]*Max-Planck-Institute for Marine Microbiology, Department of Biogeochemistry, Bremen, Germany*
[5]*University of New South Wales, School of Biological, Earth and Environmental Sciences, Australian Centre for Astrobiology, Sydney, Australia*

Paleoarchean rocks from the Pilbara Craton (Western Australia) provide a variety of evidence for early life on Earth (3.5-3.0 Ga).[1-3] However, the biological origin of potential fossils and biosignatures is still controversial, because some of the evidence can also be explained by non-biological processes.[1, 2] Further data is therefore required to "prove" the presence and diversity of life in Paleoarchean settings. Important clues on potential microbial metabolisms were obtained from detailed observations of samples from different paleoenvironments in the Pilbara. Based on detailed thin section analyses and Raman spectroscopy, promising samples were chosen for biogeochemical analyses (e.g. bulk $\delta^{13}C_{org}$). Based on these data, two different types of rocks have been selected for further geochemical investigations: (1) a sedimentary chert characterized by a primary and most likely microbial "zebra fabric" and framboid pyrite (Strelley Pool Fm; 3.35 Ga; Fig. 1a, b); (2) an unweathered black chert with fresh pyrite from a hydrothermal vein (Dresser Fm; ca. 3.48 Ga; Fig. 1c, d).

Biogeochemical characterization of kerogens from these cherts has been obtained with nano secondary ion mass spectrometry (NanoSIMS) and catalytic hydrogen pyrolysis (HyPy). NanoSIMS was used to investigate the distribution of bioelements and the respective isotope signatures with extreme high resolution (Fig. 1e-h). HyPy will be applied to sensitively release covalently-bound hydrocarbons from the geo-macromolecular organic matter (i.e. kerogen) by using high pressure and temperature in an H2 atmosphere.[4] Respective results will be discussed and evaluated with regard to the identification of potential biosignatures from different settings in these Paleoarchean rocks.

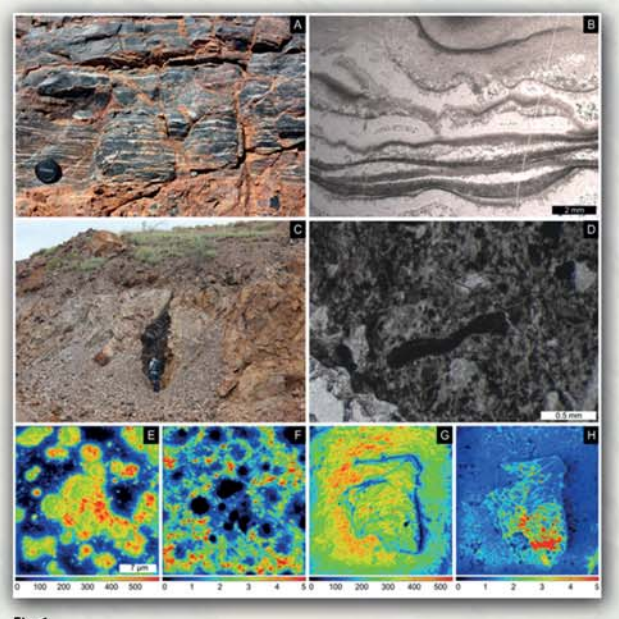


Fig. 1
Field and thin section photographs of the biogeochemically characterized cherts from the Strelley Pool Fm (A, B) and the Dresser Fm (C, D). NanoSIMS element maps of kerogens preserved in the Strelley Pool Fm (E: ^{12}C; F: ^{14}N) and the Dresser Fm (G: ^{12}C; H: ^{14}N) (F-H same scale as E).

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The organic payload of comets and a scenario for the Late Heavy Bombardment phase

Chaitanya Giri

Max Planck Institute for Solar System Research, Department Planet and Comets, Göttingen, Germany; giri@mps.mpg.de

In 2010 the Herschel Space Observatory detected a deuterium to hydrogen (D/H) ratio of 1.61 (± 0.24) × 10-4, on comet 103P/Hartley. This ratio is comparable to the D/H ratio of Earth's oceanic water which is 1.558 (± 0.001) × 10-4. 103P/Hartley is believed to originate from the Kuiper Belt region of the Solar System that extends beyond the orbit of giant planets at radii of 40-50 AU.[1] This observation hints at a possibility that comets might have delivered bulk of water and organic material from the colder confines of the outer Solar System, the Kuiper Belt, during the Late Heavy Bombardment.[2-4]

Kuiper Belt object's and comets frequently return characteristic astronomical near-infrared reflectance, reddened coloration, which possibly arises due to complex organic solids.[5-8] One synthetic analogue of cometary complex refractory organic solid is tholin.[9, 10] Experimental studies of tholin show that they are complex combinations of C–N–H molecules, ranging from low molecular mass molecules up to macromolecules readily soluble in polar solvents and very poorly soluble in nonpolar solvents.[10, 11] Laboratory measurements of molecular weights of tholin range from 100-800 Da.[12, 13] Over the past 30 years, considerable efforts have been made to try to elucidate the chemical structure and composition of tholin. However, so far they are still very poorly chemically identified and further laboratory investigation is clearly needed.

Recent investigations on tholin composition directs several sp^2 carbon allotropes in nanoscopic curved fullerenic- and planar graphene-like conformations, and microscopic turbostratic graphite and soot within its structure.[14] These observations have created new scenarios for the cometary delivery of prebiotic organics packed inside refractory carbonaceous material to early Earth during the Late Heavy Bombardment phase.

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Molecular thermometers: using ancestral sequence reconstruction to infer the history of adaptation to environmental temperature along the tree of life.

Manolo Gouy[1], Mathieu Groussin[1] & Bastien Boussau[1]

[1]*Université Lyon 1, Laboratoire de Biométrie et Biologie Evolutive, Villeurbanne, France; E-mail: manolo.gouy@univ-lyon1.fr*

It was recently recognized that the effects of environmental temperature on ancestral organisms left genetic footprints that could be uncovered in extant genomes. These effects allow to define "molecular thermometers" that relate ancestral environmental temperatures to the composition of ancestral molecules in nucleotides and amino acids. The application of molecular thermometers is therefore determined by the accuracy of the reconstruction of ancestral molecular compositions. Recent progress in the definition of probabilistic models of the evolutionary process has improved the biological realism of these models by accounting for the variation of patterns of molecular evolution among lineages. These new non-homogeneous methods allow reconstructing ancestral molecular compositions more accurately than traditional homogeneous methods. Analyses of genomic data using these tools allow attempting to reconstruct the evolutionary history of the adaptation to environmental temperatures at the scale of the tree of life. The evidence supports a mesophilic life style for LUCA, the last universal common ancestral, but hyperthermophilic life styles for LBCA and LACA, the last common ancestors of the bacterial and archaeal domains, respectively.

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Conoform stromatolite in the 3.35 Ga Strelley Pool Formation (Western Australia).

Simulating diagenesis of Precambrian banded iron formations: The fate of primary iron minerals and organic carbon

Maximilian Halama[1], Elizabeth Swanner[1] & Andreas Kappler[1]

[1]*Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany; E-mail: maximilian.halama@uni-tuebingen.de*

Precambrian banded iron formations (BIFs) were accumulated during a time when the oxygen concentration on Earth increased significantly and, therefore, are frequently used as geological archives to reconstruct the environmental conditions and their changes over time on early Earth. They are sedimentary rocks consisting of alternating iron- and silica-rich layers with a very low carbon content and the most common Fe minerals are hematite ($Fe(III)_2O_3$), magnetite ($Fe(II)Fe(III)_2O_4$), siderite ($Fe(II)CO_3$), and Fe(II)/Fe(III) silicates like stilpnomelane. The presence of Fe(II) minerals raises the question which others processes were involved in BIF sedimentation since the chemical oxidation by free oxygen in the ocean water column would lead to precipitation of Fe(III) minerals only. Processes suggested to cause Fe(II) mineral formation are the chemical precipitation directly from the water, the microbial Fe(III) reduction by Fe(III)-reducing bacteria and the abiotic reduction of Fe(III) by organic carbon during P/T-diagenesis. We are focused on the P/T-induced abiotic Fe(III) reduction. Aim of our study is to understand the processes occurring during the reduction of Fe(III) and oxidation of organic carbon by investigating the transformation of the minerals by heat and pressure, the formation of carbon-bearing gas phases and the properties of the residual solid carbon phase. Therefore, we simulated the simultaneous deposition of dead phototrophic Fe(II)-oxidizing bacteria and their metabolic Fe(III) mineral products as possible contributing factors to BIF formation. For this, we filled gold capsules with different mixtures of synthesized Fe(III) minerals and microbial biomass and incubated them at 170 °C and 1.2 kbar for 14 days to simulate low-metamorphic conditions. After incubation, we identified and quantified the gaseous compounds that were formed during the reaction (CO and CO_2) by gas chromatography-mass spectrometry. Up to 10 % and 8 % of the organic carbon, which was in the organic carbon source before incubation, were found in CO and CO_2, respectively, after incubation. We identified the mineralogy utilizing various analytical techniques including x-ray diffraction (XRD), Mössbauer spectroscopy and reflected-light microscopy, and determined the Fe(II)/Fe(III) ratio in the bulk sample photometrically after acidic dissolution of all Fe minerals. The mineralogical results show a siderite formation up to 14 %, whereas the Fe(II)/Fe(tot) ratio in the same sample is 29 %. Magnetite formation might be occurred as well which is supported by reflected-light microscopy, however, it is not detected by XRD and Mössbauer spectroscopy. The residue of the biomass was identified as kerogen by Raman spectroscopy and its carbon isotope composition was determined by isotope ratio mass spectrometry. Carbon isotopes ratios obtained by mass spectrometric measurements of the kerogens revealed an enrichment of ^{13}C in the residual carbon phase up to 2.35 ‰ (VPDB). The results from the mineralogy and isotope analysis are in agreement with the model about formation of siderite in BIFs which is depleted in ^{13}C by incorporation of light carbon isotopes from organic matter. Based on our data, the abiotic Fe(III) reduction by organic carbon induced during P/T-diagenesis of BIFs has potentially occurred, which would support the model about the presence of microorganisms aside the continental shelf regions in Archean oceans.

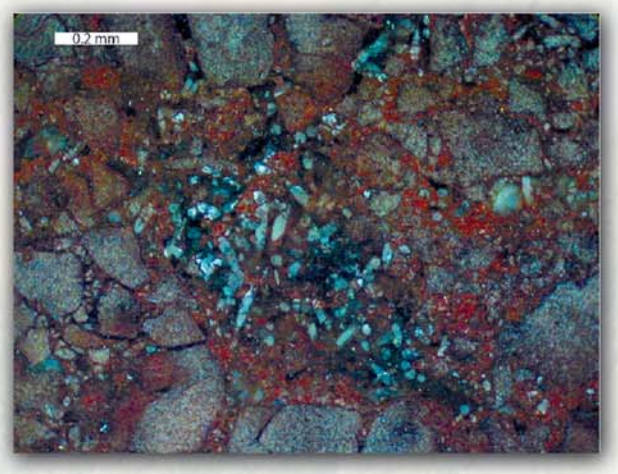

Fig. 1
Siderite grains (light grey) in black matrix and surrounded by hematite (granular-looking dark grey and red) formed during incubation of a mixture of ferrihydrite [$Fe(OH)_3$] and microbial biomass at 170 °C and 1.2 kbar.

Steroid biomarkers throughout the Precambrian yield a fresh look on eukaryotic evolution

Christian Hallmann[1,2]

[1]*Max-Planck-Institute for Biogeochemistry, Organic Paleobiogeochemistry Group, Jena, Germany; E-Mail: challman@bgc-jena.mpg.de*
[2]*University of Bremen, Center for Marine and Environmental Sciences (MARUM), Bremen, Germany*

Eukaryotic algae play a key role in primary production within the contemporary ocean and cover the majority of organic matter (OM) fluxes to higher trophic levels and the ocean interior[e.g. 1] thereby carrying large responsibility for maintenance of the biological pump and a carbon cycle equilibrium.[1,2] It is likely that this significant role would have been covered by eukaryotes ever since they rose to ecological significance, and that their mere evolutionary emergence would have had a profound effect on biogeochemical cycling. Yet the timing of these events has not been satisfactorily constrained. In particular the first appearance of eukaryotes represents a question surrounded by much debate. The discrepancy we observe between the oldest eukaryotic microfossils (~1.5 Ga[3]) in the sedimentary record and their estimated emergence based on molecular clock studies (1.7-1.9 Ga[4]) might be attributable to global Mesoproterozoic ocean chemistry, where more widespread zones of bottom-water anoxia and euxinia caused drawdown of the global marine molybdenum pool[5] driving eukaryotes to occupy environmental niches characterized by poor taphonomic potential.[3] But apart from fossilized cell envelopes, eukaryotic evolutionary patterns can also be assessed on a molecular level. All eukaryotes engage in aerobiosis, implying that they would not have emerged before the advent of oxygenic photosynthesis, and rely on the production (or, in rare cases, dietary uptake) of sterol molecules for homeostasis.[6] The biosynthesis of sterols in itself is an oxygen-intensive process[7] that is unlikely to have emerged prior to the advent of oxygenic photosynthesis in an ancestral cyanobacterium. When preserved in sediments, sterols diagenetically convert to steranes, which can be employed as unambiguous evidence for the existence of the steroid biosynthetic pathway, molecular oxygen and- quite likely- eukaryotic organisms at the time of deposition. At the turn of the last century, hopanes and steranes were reported from subgreenshist facies Archean sediments[8] and used as an argument for the early evolution of eukaryotes and cyanobacteria (in case of eukaryotes ~1.2 Ga earlier than established by the microfossil record). In the following years these results were corroborated by additional studies[9-14] and the proposed evolutionary dates had been adopted by a good portion of the geobiological community. Although molecular abundance heterogeneities in different parts of ancient core samples and stable carbon isotopic mismatches between biomarker analytes and their corresponding kerogens increasingly raised contamination concerns[e.g. 15] the question of biomarker indigeneity or contamination could not be unequivocally resolved with existing sample material. In 2012 we have drilled three holes on the Pilbara Craton of northwestern Australia (Agouron Institute Drilling Program) under unprecedentedly clean conditions and were able to establish the absence of any diagnostic hydrocarbon biomarkers. Results were reproduced across 4 laboratories that studied cuts from the same core samples and, based on the distribution of polyaromatic hydrocarbons and diamondoid molecules, revealed a significantly higher thermal maturity of the organic matter than previously assumed. These results thus nullify previous claims and revert to 1.5 Ga acritarchs as the currently oldest evidence for eukaryotes on Earth. Interestingly, a growing number of studies[e.g. 16] have been reporting the absence of eukaryotic steroid biomarkers from carbonates and black shales in the 1.7-1.0 Ga age range that have experienced a thermal overprint too low for the destructive cracking of polycyclic terpenoids. The latter claim is substantiated by the presence of structurally similar hopanoids of bacterial origin in many of those samples. Some attribute this observation to extensive heterotrophic reworking of pelagic organic matter on vast and widespread benthic microbial mats[17] but the alternative explanation is simply that eukaryotes were just not of ecological significance at this point in Earth history. Even during the subsequent Neoproterozoic Era, when eukaryotic acritarchs become more abundant in sediments, our understanding of the environmental role played by eukaryotes is minimal. Previously reported full suites of C27-C29 steranes in rocks ~750 Ma in age appear to be incorrect, and we are finding a growing number of sediments deposited between ~750 Ma and ~630 Ma (i.e. until after the Marinoan glacial event) whose steroid inventory is represented solely by cholestanoic components. Then, during the later Ediacaran, a strong global prominence of C29 steroids becomes evident[e.g. 18] before settling to more normal Phanerozoic-like distribution in the Early to Middle Cambrian. What does this mean for the evolution of the Earth system? In this presentation I will cover the above results in greater detail and hypothesize on the role that the rise of eukaryotes to ecological prominence might has played on the Neoproterozoic carbon cycle instability, the oxygenation of deep oceanic waters and the mere possibility of plunging Earth into Snowball-like glacial states.

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Silicified microbial mats in the 3.35 Ga Strelley Pool Formation (Western Australia).

Dating the origin of life with molecular clocks and other evidence

S. Blair Hedges

Temple University, Center for Biodiversity, Philadelphia, USA; E-Mail: sbh@temple.edu

The earliest events in the history of life have been the most difficult to study because there is little evidence in the fossil record and great uncertainty in the geologic and climatic records at that time. One hopeful prospect for information about the origin of life has been the molecular record, and particularly the ability to date events in history with molecular clocks from DNA and protein sequence data. The moon-forming event at 4.5 billion years ago (Ga) provides the earliest time constraint for the origin of life on Earth, while the first widely accepted fossils at 3.5 Ga provide the latest time constraint. Working with other non-biological and biological evidence, including molecular clocks, it is possible to narrow down the probable time for the origin of life within this one billion year period. These efforts will be discussed at the workshop.

Landscape of the North Pole region (Western Australia) with characteristically exposed hydrothermal veins.

Biomineral formation by a thermophilic Archaeon as a model for processes in Archean cherts

Michael Hoppert[1], Dominik Mühlen[1] & Joachim Reitner[2]

[1]Georg-August-University of Göttingen, Institute of Microbiology and Genetics, Department of General Microbiology, Göttingen, Germany; E-mail: mhopper@gwdg.de
[2]Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany

Numerous microfossils of single cells or microbial mats have been described for Paleoproterozoic environments. In contrast, Archean fossil records are ambiguous and may be also interpreted as non-biogenic. In this respect, chemical fossils of all kinds may be helpful to verify or falsify these structures as of microbial origin. Besides organic molecules (that may have been all degraded or overprinted), inorganic molecules may, along with other biomarkers, be valuable for identifying microbial activity. Inorganic minerals are more stable in appropriate settings (e.g. in cherts) than organic molecules, and less susceptible to overprinting. It is obvious that the origin of these minerals has to be evaluated carefully. (Nearly) all inorganic compounds may be of abiogenic origin. Frequently, microorganisms just provide an organic matrix for formation of minerals that may also precipitate in the same setting without an organic "template". Model environments, either natural or artificial, are important for understanding generation and deposition of putative biomarker minerals. Model microorganisms involved in the precipitation of putative biomarker minerals may be helpful to distinguish between biogenic and abiogenic processes.

Several anaerobic Bacteria and Archaea produce the manganese carbonate rhodochrosite. The process is conducted at redox potentials between microbial denitrification and Fe(III) reduction. In recent anoxic sediments rhodochrosite derives mainly from the reduction of Mn(IV) compounds by microbial anaerobic respiration. Large amounts of Mn(IV) oxides are generated by various microbial processes, all requiring an oxygenated atmosphere.[1, 2] Also microbial nitrate-dependent oxidation of manganese is possible, though hitherto widely unknown.[3] Thus the insoluble, but amorphous MnO_2 and its derivatives (on average $MnO_{1.7}$) are readily available for anaerobic respiration in the sediment, some millimeters below the oxidizing surface. Though Archean environments were anoxic and strongly influenced by hydrothermal vents, it must be assumed that oxygen oases existed and Mn(IV) oxides as electron acceptors for anaerobic respiration may have been formed long before atmospheric oxygenation. In addition, biogenic pathways for manganese oxidation under anaerobic conditions may be possible. Johnson et al.[4] considered that Mn(IV) oxide derived, under anoxic conditions of the early Archean, from pre-oxygenic photosynthesis with Mn(II) as an electron donor for a primitive anoxygenic photosynthesis. Manganese redox cycling will then continue by reduction of Mn(IV) to Mn(II) (leading to $MnCO_3$ precipitation) by anaerobic respiration. The putative photosynthetic manganese-dependent redox cycling is a reasonable derivative of analogous recent cycles with iron and sulfur compounds, which are oxidized by anoxygenic photosynthesis (producing biomass) and are reduced by anaerobic respiration, leading to degradation of organic compounds. Presently, no photosynthetic process with Mn(IV) as external electron source is known. However, protein-bound manganese ions at different redox stages are forming the reactive center of the water splitting, oxygen-evolving complex and it is reasonable to assume that free reduced manganese ions have been the electron donors for a proto-oxygen evolving complex[4]. After all, manganese redox cycling might have been possible even before the onset of oxygenic photosynthesis. Hence, there are several ways how rhodochrosite could have been formed biogenically and deposited in Archean cherts. The hyperthermophilic archaeon *Pyrobaculum islandicum* produces rhodochrosite biominerals during growth on hydrogen and organic compounds and may be a putative model organism for the reduction of Mn(IV) in these settings.

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The role of microbial iron oxidation and iron reduction in deposition and transformation of Precambrian Banded Iron Formations

Andreas Kappler[1] & Kurt Konhauser[2]

[1]*Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany; E-mail: andreas.kappler@uni-tuebingen.de*
[2]*University of Alberta, Department of Earth & Atmospheric Sciences, Edmonton, Canada*

Banded Iron Formations (BIFs, Fig. 1) are iron rich (~20-40 % Fe) and siliceous (~40-50 % SiO_2) sedimentary deposits that precipitated throughout much of the late Archean (2.7-2.5 Ga) and Paleoproterozoic (2.5-1.8 Ga). The study of these formations is highly relevant as their deposition bridges the expanse of geological time in which oxygen arose, first in the oceans around 2.7 Ga[e.g. 1], and then the atmosphere between 2.45-2.32 Ga during the Great Oxidation Event (GOE)[e.g. 2]. BIFs are characteristically laminated, with alternating Fe-rich and Si-rich layers. Banding can be observed on a wide range of scales, from coarse macrobands (meters in thickness) to mesobands (centimeter-thick units) to millimeter and submillimeter layers. Among the latter is the wide variety of varve-like repetitive laminae, known as microbands.

The mineralogy of the least metamorphosed BIFs consists of chert, magnetite, hematite, carbonates (siderite, dolomite-ankerite), greenalite, stilpnomelane and riebeckite[3, 4]: the presence of both ferric and ferrous minerals gives BIFs an average oxidation state of $Fe^{2.4+}$.[5] It is generally agreed that none of the minerals in BIF are primary, but that instead, the minerals reflect both diagenetic and metamorphic overprinting. For instance, the primary iron minerals were most likely ferric hydroxide ($Fe(OH)_3$), greenalite ($(Fe)_3Si_2O_5(OH)_4$), and siderite ($FeCO_3$).

It is becoming increasingly accepted that microorganisms were involved in the primary oxidation of Fe(II) to Fe(III) in BIFs.[6-8] Two possible roles for bacteria are envisioned. The first is based on the production of O_2 by cyanobacteria. These photoautotrophs would have passively induced the precipitation of ferric hydroxide through the formation of O_2 followed by an indirect, abiotic oxidation of the Fe(II) by the cyanobacterially produced O_2. Other bacteria may have played a more active role in Fe(II) oxidation. For instance, Holm[9] speculated that oxidation of dissolved Fe(II) by chemolithoautotrophic bacteria (e.g. *Gallionella ferruginea*) would have been kinetically favored in an ocean with limited free O_2 because abiological oxidation of Fe(II) at neutral pH is slow under microoxic conditions. Meanwhile, Hartman[10] first suggested that anoxygenic photosynthetic Fe(II)-oxidizing bacteria may have coupled the C and Fe cycles prior to the evolution of oxygenic photosynthesis. Since then, a number of experimental studies have indeed confirmed that various purple and green phototrophic bacteria can use Fe(II) as a reductant for CO_2 fixation[11] and could have actively contributed to BIF deposition[7].

The biological story on BIF, however, tends to neglect what happens to the organic remains and ferric hydroxide particles as they settle through the water column and become deposited at the sea floor. Given that the bulk water column was anoxic, perhaps with the exception of an upper layer of oxygenated waters above the chemocline of a stratified ocean, the ferric hydroxide would have represented a favorable electron acceptor for the oxidation of the cellular organic remains. Certainly, the capacity of extant hyperthermophilic Bacteria and Archaea to reduce Fe(III), and the recent observations of highly negative $\delta^{56}Fe$ values in magnetite-rich BIF samples as old as 2.9 Ga[12], with comparable negative fractionations as observed in experimental cultures with Fe(III)-reducing bacteria[e.g. 13], point towards the antiquity of such an anaerobic respiratory pathway. Significantly, coupling the reduction of Fe(III) minerals to the oxidation of organic matter not only explains the low content of organic carbon in the BIFs (<0.5 wt%)[14], but it also explains the abundance of light carbon isotopic signatures associated with the interlayered carbonate minerals[e.g. 15].

In summary, it appears as the mineralogy observed nowadays in BIF rocks is a result of abiogenic and biogenic Fe redox transformation followed by abiotic diagenesis at high pressures and temperatures over geological time. In this presentation I will give an overview about the potential microbial processes involved in Fe-mineral formation and transformation during BIF deposition and initial diagenesis.

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Fig. 1: Banded Iron Formation, South Africa, Kuruman area (photo by A. Kappler).

From RNA to DNA as the genetic storage medium – the history of a stepwise takeover

Wilfried Kramer[1] & Hans-Joachim Fritz[2]

[1]*Georg-August-University of Göttingen, Institute of Microbiology and Genetics, Department of Molecular Genetics, Göttingen, Germany*
[2]*Georg-August-University of Göttingen, Courant Research Centre Geobiology, Göttingen, Germany; E-Mail: hansj.fritz@gmail.com*

It is generally believed that DNA as the storage medium of genetic information was preceded by RNA and the evolutionary period before the time point of takeover is called the RNA world, which can be sub-divided into an (early) "RNA alone" and a (later) "RNA/protein" world. DNA differs from RNA in several structural characteristics: *(i)* lack of 2' hydroxy group, *(ii)* double strandedness, *(iii)* use of T instead of U as the base-pairing partner of A. Since it seems unlikely that all three differences were introduced at the same time, the question arises as to the order of the individual steps. In the talk it will be argued that the same selective pressure was operating for all three changes, namely the limitation of genome size due to hydrolytic attack on the respective nucleic acid, targeting three different sites of different hydrolytic vulnerability. This assumption, when combined with known rate constants of the respective hydrolysis reactions, unequivocally delineates the order in which the three steps occured. The postulated sequence of events is supported by the structure of present-day DNA repair mechanisms.

Oldest known stromatolites of the world (3.49 Ga, Dresser Formation, Western Australia).

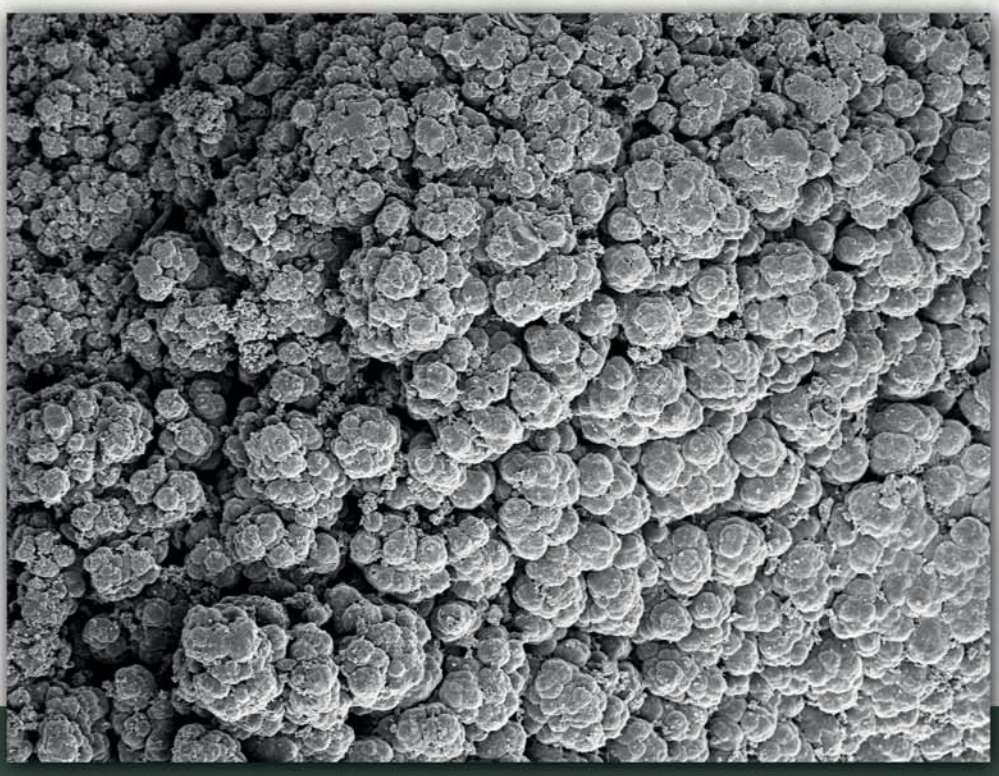
Abiotic pathways for the formation of reduced carbon on the early Earth

Tom McCollom

University of Colorado Boulder, Laboratory for Atmospheric and Space Physics, Boulder, USA; E-Mail: tom.mccollom@lasp.colorado.edu

Many scientists currently believe that life had become widely established on Earth by 3.5 billion years ago, and possibly long before that time. This belief is based largely on reduced carbon deposits found in ancient rocks whose morphology and isotopic composition are consistent with a biological origin. At the same time, however, there exist plausible non-biological pathways that can explain the occurrence of many of these carbon deposits, leading to continuing uncertainty over the distribution of life on the early Earth and the source of reduced carbon in ancient rocks. Effort to resolve this uncertainty could be enhanced by a better understanding of the characteristics of reduced carbon compounds formed by abiotic and biotic processes. Towards this goal, I will present results of laboratory experiments that explore reaction pathways for the abiotic formation of reduced carbon in geologic environments. The well-known Fischer-Tropsch synthesis and related processes generate organic matter that can reproduce some characteristics of ancient reduced carbon including its isotopic composition, but so far it has proven difficult to make these reactions proceed under geologically realistic conditions. Current research is focusing on the formation of insoluble reduced carbon deposits during serpentinization and other geologic processes, which may form through direct interaction of inorganic carbon with iron-bearing minerals without the participation of soluble organic intermediates.

Condensed artificial tholin aggregates (SEM photo).



Experimental diagenesis of modern Fe(II)-oxidizing bacteria to help understanding the fossil record

Aude Picard[1, 2], Andreas Kappler[1], Gregor Schmid[1], Luca Quaroni[3, 4] & Martin Obst[1]

[1]*Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany; E-mail: aude.picard@uni.tuebingen.de*
[2]*Harvard University, Department of Organismic and Evolutionary Biology, Cambridge, USA*
[3]*Paul Scherrer Institute, Infrared Group, Villigen, Switzerland*
[4]*ETH Zurich & University of Zurich, Functional Genomics Center Zurich, Zurich, Switzerland*

As a result of Fe(II) oxidation under low O_2 concentrations, some microaerophilic Fe(II)-oxidizing bacteria (FeOB) produce organo-mineral structures of unique morphology and composition – so called twisted stalks. If these structures can withstand diagenetic alterations, they could record ancient FeOB activity and serve as proxies for palaeoenvironmental oxygen concentrations. However, temperature (T) and pressure (P) conditions under which twisted stalks are preserved for utilization as biosignatures for FeOB have not been determined. We used spectroscopy and analytical microscopy to evaluate if – and what kind of – transformations occurred in the twisted stalks through experimental diagenesis, at T-P conditions corresponding to diagenetic conditions that some late Archean iron formations (IF) experienced. The twisted morphology of the stalks was preserved at 250°C - 140 MPa. Hematite and magnetite formed from ferrihydrite at 170°C - 120 MPa. Mineral textures at the surface of the stalks evolved as a function of T-P conditions. The organic matrix, mainly composed of long-chain saturated aliphatic compounds, was preserved at all investigated T-P conditions, likely through its association with Fe minerals. We conclude that Fe biomineralization helps preserving microbial extracellular structures under diagenetic conditions and we define T-P-dependent morphological, mineralogical and spectroscopic signatures for FeOB activity. We also provide experimental evidence that biosignatures and microfossils indicative of FeOB could be retained in late Archean IF.

The Marble Bar Chert Member (3.45 Ga, Western Australia).

Early Archean carbonates on early Earth - microbial biosignature versus hydrothermal origin

Joachim Reitner[1], Jan-Peter Duda[1] , Nadine Schäfer[1] , Martin Van Kranendonk[2], Michael Hoppert[3], Franziska Wilsky[4] & Bent Hansen[4]

[1]*Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany; E-mail: reitne@gwdg.de*
[2]*University of New South Wales, School of Biological, Earth and Environmental Sciences, Australian Centre for Astrobiology, Sydney, Australia*
[3]*Georg-August-University of Göttingen, Institute of Microbiology and Genetics, Department of General Microbiology, Göttingen, Germany*
[4]*Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany*

Early Archean carbonates from the Pilbara (Western Australia; WA) and the Barberton Greenstone Belt (South Africa; SA) are almost the oldest known in Earth history and compositionally variable. Their origin is mostly unclear- formed biologically and/or abiologically. Archean environments were anoxic and strongly influenced by hydrothermal vents. Few stromatolites (e.g. 3.35 Ga Strelley Pool Fm, WA) are still preserved as a dolomite, indicating microbial growth in the setting. These dolomites are zoned and exhibit a strong cathodoluminescence (Cl). The cores of the dolomites, however, are non-luminescent and represent the primary precipitate. REE+Y analyses of the dolomite cores (negative Ce anomaly, positive Y anomaly) show patterns similar to modern microbialites and exhibit $\delta^{13}C_{VPDB}$ values (ca. +3 ‰) that are in accordance with carbonates deposited through photoautotrophy. These geochemical characteristics are strikingly different to those of hydrothermal carbonates (kutnohorite and ankerite in the 3.5 Ga Dresser Fm, WA), which exhibit high Fe, Sr and Ba concentrations, REE+Y pattern typical for a hydrothermal source (positive Eu anomaly), and distinct $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{SMOW}$ values (-6 ‰ and +21 ‰, respectively). Calcite precipitated within inter pillow spaces of the ca. 3.46 Ga Apex basalt exhibit $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{SMOW}$ values (0 ‰ and +13.5 ‰, respectively) nearly similar to modern marine settings. The most intriguing Archean carbonates, however, are linked to small organic flakes (100-200 µm) within Pilbara hydrothermal chert veins (Fig. 1a) and silicified 3.25 Ga sedimentary rocks of the Fig Tree Group (SA) (Fig. 1b). The flakes have $\delta^{13}C_{VPDB}$ values of ca. -25 to -30 ‰ and are commonly associated with small (10-20 µm), high-luminescent Mn-rich carbonates as e.g. rhodochrosite. Hyperthermophile archaea like *Pyrobaculum islandicum* were reported to be able to reduce MnO_4 at 100°C while precipitating rhodochrosite[1] which was confirmed by own experiments (Fig. 1c). Rhodochrosite and further Mn-rich carbonates as e.g. kutnohorite may therefore be in analogy the product of archaeal activity within the chert veins and silicified Fig Tree sediments. While the validity as a microbial biosignature remains to be proven, multiple lines of evidence argue for early Archean carbonates as important environmental archives of microbial activity on early Earth.

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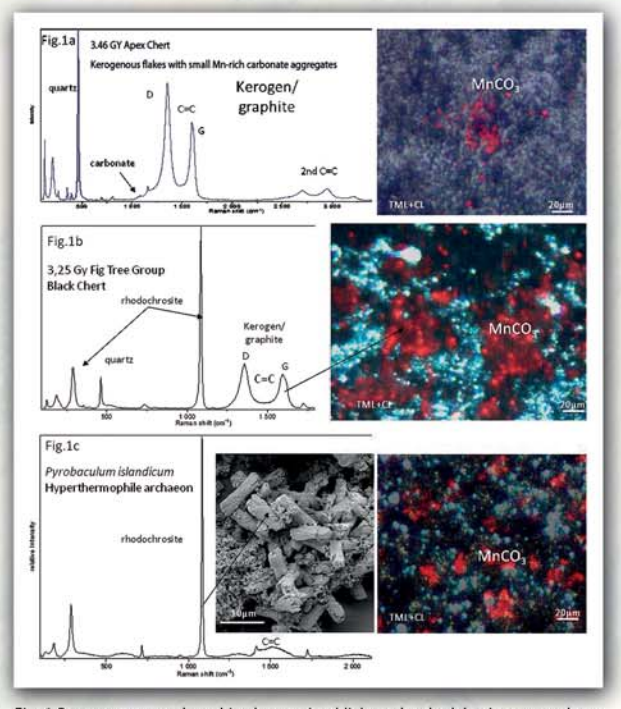

Fig. 1 Raman spectra and combined transmitted light and cathodoluminescence photographs of carbonate minerals. A: Kerogenous flakes in the Apex Chert are covered with small Mn-rich luminescent carbonate aggregates. B: Kerogenous material in the Fig Tree Group is covered by strongly luminescent small rhodochrosite crystals often arranged in rows. C: Dumbbell-shaped rhodochrosite crystals formed by the hyperthermophile archaeon *Pyrobaculum islandicum* in an anaerobic culture at ca. 100°C. Note that newly formed rhodochrosite aggregates exhibit also a strong cathodoluminescence.

The evolution of prokaryotic multicellularity and the oxygenation of Earth

Bettina E. Schirrmeister

University of Bristol, School of Earth Sciences, Bristol, United Kingdom; E-Mail: bettina.schirrmeister@bristol.ac.uk

The evolution of multicellularity has been considered one of the major transitions in the history of life[1], changing the confines on which selection may act upon and serving as the first step towards the evolution of complex life, such as animals and land plants. Simple forms of multicellularity, however, originated not once, but multiple times independently in Eu- and Prokaryotes[2] and can be dated back as far as life itself. Fossil remains of multicellular prokaryotes ("tubular filaments") have been found 3.4 billion year old rock formations.[3]

One of the most important modern phyla where various forms of multicellularity have evolved are cyanobacteria, previously known as blue-green algae. Cyanobacteria are unique among prokaryotes, as they (i) are among the oldest organisms on Earth, (ii) showing an impressive morphological diversity for bacteria, (iii) obtain a extremely well preserved fossil record (for prokaryotes), and (iv) are the only organism known, in which oxygenic photosynthesis has originated. More than 2.4 billion years ago they are made responsible for the rise of atmospheric oxygen, the so called "Great Oxidation Event" (GOE) one of the most dramatic environmental changes in the history of Earth, enabling the evolution for aerobic life as we know it today. Despite their importance for the co-evolution of early life and Earth, questions regarding the origin of cyanobacteria and their various morphotypes remain.

To infer the evolutionary history of this versatile phylum I applied phylogenetic analyses of cyanobacterial ribosomal RNA sequences to reconstruct trees, ancestral character states and divergence times using Maximum likelihood and Bayesian methods. A 1,220 taxa rich Maximum Likelihood phylogeny was reconstructed from which a subset of cyanobacterial strains was chosen cover the entire known diversity of this group. Results of phylogenetic analyses that were conducted on this subset are presented in Fig. 1. Multicellularity originated very early during the evolutionary history of cyanobacteria and was, subsequently, lost several times and regained at least once within a clade of unicellular taxa.[4] The majority of living taxa, including most unicellular forms, are, therefore, descendants of an ancient multicellular lineage. Estimations of divergence times with a Bayesian relaxed clock, based on eight differently calibrated analyses, all point towards an origin of cyanobacteria in the Archean Eon long before the accumulation of atmospheric oxygen. The first transition to multicellularity in cyanobacteria occurred before or at the onset of the GOE.[5] For cyanobacteria, multicellularity could have provided some fitness advantage helping them to become more abundant and consequently raising oxygen levels.

Recent phylogenomic studies based on 755 protein sequences conducted on 64 cyanobacterial genomes confirm the existence of an ancient multicellular lineage in cyanobacteria (own unpublished data). Further phylogenetic research on the evolution of multicellularity within Prokaryotes in comparison to the Precambrian fossil record suggest separate origins of multicellularity for different prokaryotic phyla. The earliest transitions to multicellular growth seem to have occurred within Actinobacteria, Chloroflexi and Cyanobacteria, whereas multicellular taxa within Bacteroidetes and Proteobacteria, such as *Beggiatoa*, have much more recent evolutionary origins.

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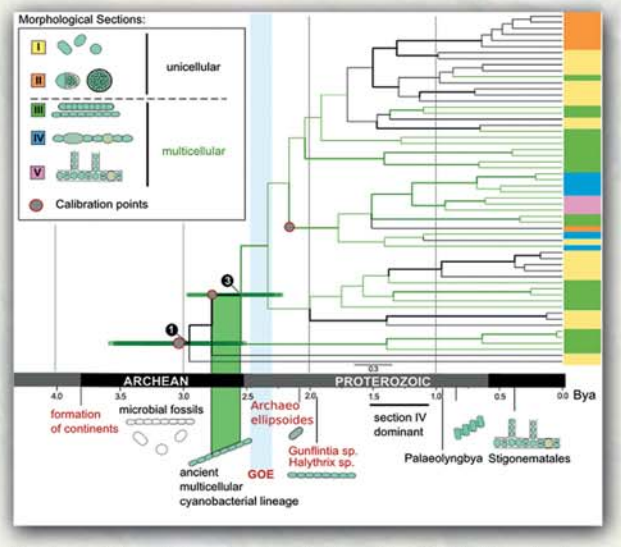

Fig. 1 The evolutionary history of cyanobacteria. Time calibrated 16S rRNA Bayesian phylogeny of cyanobacteria displaying divergence time estimates and the evolution of multicellularity (green branches). Branches with posterior probabilities >0.9 in all analyses are presented as thick lines. Gray circles mark points used for calibration of the tree. Schematic drawings of cyanobacterial fossils are provided under the timeline, with the ones used for calibration of the tree marked in red. Our results indicate that multicellularity originated before or at the beginning of the GOE (green shade; node 3). On node 1 and node 3.95 % highest posterior density of estimated ages are shown. Original figure presented in.[5]

New approach towards determining temperature isotopic composition of ancient oceans using high precision $\delta^{17}O$ and $\delta^{18}O$ analysis of cherts

Sukanya Sengupta[1], Andreas Pack[1], François Robert[2], Joachim Reitner[3], Zachary Sharp[4] & Daniel Herwartz[5]

[1]*Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany; E-mail: ssengup@gwdg.de*
[2]*Muséum National d'Histoire Naturelle, Paris, France*
[3]*Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany;*
[4]*University of New Mexico, Department of Earth and Planetary Sciences, Albuquerque, USA*
[5]*University of Köln, Institute for Geology and Mineralogy, Köln, Germany*

The ocean water temperature and/or the $\delta^{18}O$ composition over the past 4 Ga is a highly debated issue in Earth sciences. Different types of chemical sediments, like cherts, carbonates and phosphates, believed to have been precipitated in equilibrium with seawater over the ages, have been studied to solve this puzzle. These studies have shown a secular trend of progressively decreasing $\delta^{18}O$ of sediments with increasing age. This observation can be interpreted in different ways. The Archean oceans were either very hot (up to 80°C[1]) or had a significantly low $\delta^{18}O$ (e.g. -12 ‰[2]). A third possibility is that the observed low $\delta^{18}O$ of sediments are a result of diagenesis. We address this classical problem using high-precision triple O isotope ratios of cherts.

Pack & Herwartz[3] have resolved mass dependent variations in $\Delta^{17}O$ in terrestrial rocks that are related to high- and low-T fractionation processes and reservoir mixing. We modify the $\theta_{silica\text{-}water}$-temperature relation defined by them and apply this to interpret our chert data. The terms $\theta_{A\text{-}B}$, for two phases in equilibrium with each other, and $\Delta^{17}O$ are defined as follows:

$$\alpha^{17O/16O}_{A\text{-}B} = \left(\alpha^{18O/16O}_{A\text{-}B}\right)^{\theta_{A\text{-}B}} \qquad \text{(Eq.1)}$$

$$\Delta^{17}O^{sample} = 1000Ln\left(\frac{\delta^{18}O_{SMOW}}{1000}+1\right) - 0.5305 \times 1000Ln\left(\frac{\delta^{17}O_{SMOW}}{1000}+1\right) \qquad \text{(Eq. 2)}$$

We have analyzed Archean, Proterozoic, Phanerozoic and modern cherts from different locations. The samples were fluorinated using BrF_5 or F_2 by either in-situ laser fluorination or in conventional Ni reactors. The liberated oxygen was measured in the dual inlet mode of the MAT253 mass spectrometer. The precision in $\Delta^{17}O$ was about ±10-15 ppm (1σSD).

The trend of decreasing $\delta^{18}O$ with increasing age is found to be followed by decreasing $\delta^{17}O$ values as well. The Archean cherts have $\delta^{18}O$ of ca. +16 ‰ and a $\Delta^{17}O$ of ~ –140 ppm. Phanerozoic cherts have $\delta^{18}O$ of about +30 ‰ and $\Delta^{17}O$ around -250 ppm. The composition of the Proterozoic cherts falls in between these two in the triple isotope space (Fig. 1)

We will discuss the results with respect to the temperature and $\delta^{18}O$ of Precambrian and Archean seawater.

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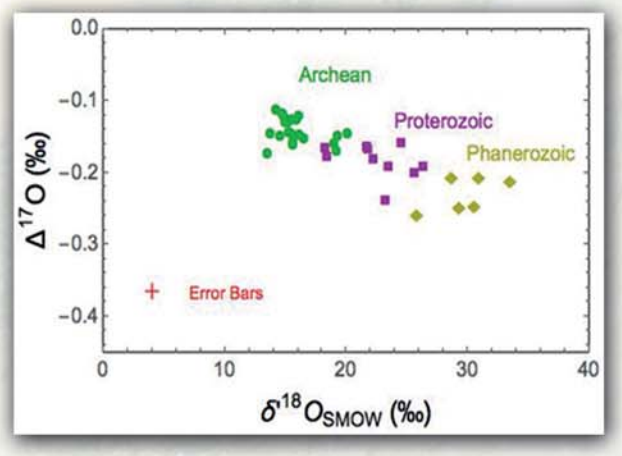

Fig. 1 Triple oxygen isotope data of cherts from different locations and geologic ages. Cherts show a secular trend of decreasing $\delta^{18}O$ and $\delta^{17}O$ with incrasing age, which means an increasing $\Delta^{17}O$ with age.

What do prions, viruses and viroids reveal about the formation of life on Earth ?

Andrew Steele

Carnegie Institution of Washington, Geophysical Laboratory, Washington D.C., USA; E-Mail: asteele@carnegiescience.edu

Reconstructing the processes and reactions that led to the origin of life on Earth has proved elusive. While many hypotheses have been proposed certain key stages in the origin of life remain a major hurdle. In recent years there has been a revolution in our understanding of the interaction of "simple" protein and nucleic acid constructs and their role in disease, cell regulation and evolution. Alongside fungi, bacteria and viruses, new disease factors such as prions and viroids have expanded our understanding of the variation and complexity of the interactions of small molecules with proteins and nucleic acids. While these molecules have been extensively studied for their effects in disease of animals and plants, their discovery and mode of operation may well give fundamental insights into the start of life on Earth. In this abstract I seek only to stimulate thought and debate on what are the fundamental properties of these structures that may play a role in the origin of life. Furthermore, I will discuss what areas of investigation may yield a better understanding of the interactions that led to life. While viruses, prions and viroids all need a host to propagate, they all show fundamental properties that if a host was not present may have played a role in increasing complexity and beneficial interactions between proteins and nucleic acids that led to the first cells.

In 2002, for the first time an infective virus has been synthesized from pure chemicals.[1] The properties of self-assembly would be key in the formation of putative pre-biotic DNA, protein constructs. The finding that viruses possibly predated the formation of the three domains of life has led to the "virus first" hypothesis.[2] However, the rules and interactions that led to the first viral like particles must have been a result of the formation of the first cells. This possibility can only have taken place if the mechanism of protein formation and interaction with nucleic acids, had already evolved and was conserved. The mechanisms of self-assembly are still not well understood, but recent research showing that size of RNA strand dictates the size of capsid formed shows that there is a fundamental relationship between nucleic acids and proteins in the conservation of form. While a structural interaction between nucleic acid and protein is well understood one question that remains is the feedback between nucleic acids and amino acids in the formation of the genetic code. Viruses, prions and viroids provide a pool of non-life interactions that in some way could be described as prebiotic.

Prions induce refolding of non-disease forms to a disease form without changing the primary structure of the protein. They contain specific protein motifs that catalyse the change of non-disease to disease state. While pure prion protein itself can propagate the formation of disease particles in-vitro, interactions with RNA considerably increase the yield of disease particles.[3] Furthermore, it appears that certain prions can also act as DNA chaperones similar to HIV-1 capsid protein.[4] The nature of these interactions appears to indicate that there is a feedback loop in form between simple nucleic acids and protein constructs that is fundamental to the functioning of both. This feedback loop confers advantages to both sets of molecular constructs including propagation and survivability. For example, the disease state of human PrP prion survives autoclaving. In this case prion folding confers a survivability trait that converts a protein that cannot survive above 60°C to one that survives at similar temperatures to that seen in hydrothermal systems. One problem with the formation of DNA and RNA in such environments is their survival in that system. Interactions between primitive prion like particles and RNA for example benefits both constructs. Survivability in harsh conditions for proto RNA constructs which in turn catalyze proto-prion propagation. It would seem that the most efficient way to form a genetic code is to ensure that protein / nucleic acid interactions are enabled, and continue in changing environments that both nurture and challenge the relationship. From such interactions feedback loops can be established. Given the importance of shape and its conservation in biology, it suggests that this property is fundamental in the formation of life on Earth. Therefore, prion, nucleic acids constructs and interactions would be key in generating a combinatorial system of random / semi-random orientations and interactions to generate more specific interactions that conveyed a beneficial trait.

While viruses, viroids and prions are almost exclusively studied for their disease causing properties and usually considered in such a light, the study of bacteria was once solely the provenance of medical microbiology. Study of bacteria in the environment is a relatively new field in comparison but has led to our understanding of the limits to life on Earth in environment and time. It must also be so for the study of proto-life constructs. The environmental presence and interactions of these particles are relatively unknown but may be just as fundamental to our understanding of how life started on Earth.

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The role of Fe in modulating Earth's oxygenation

Elizabeth D. Swanner[1] & Andreas Kappler[1]

[1]*Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany; E-mail: elizabeth.swanner@ifg.uni-tuebingen.de*

Multiple lines of evidence indicate temporally and spatially limited oxygen production by at least 3.0 Ga[1,2], prior to the Great Oxidation Multiple lines of evidence indicate temporally and spatially limited oxygen production by at least 3.0 Ga[1,2], prior to the Great Oxidation Event (GOE) at ca. 2.4-2.32 Ga[3], in which oxygen began its irreversible rise in the atmosphere. We ask whether early cyanobacteria were initially limited in their ability to produce oxygen by geochemical conditions present in aqueous Archean habitats, which might explain the evidence for episodic and protracted rise of oxygen during the Archean. Using a modern marine cyanobacterium, *Synechococcus* PCC 7002, incubated in initially anoxic conditions with tens to thousands of µM Fe(II), we documented the production of toxic reactive oxygen species (ROS). In growth experiments, this toxicity, resulting from abiotic reactions between Fe(II) and photosynthetically produced oxygen, reduced growth rates and the capacity of cyanobacteria to produce oxygen. These results are significant in light of evidence for Fe(II)-rich Archean oceans.

Predominant hypotheses indicate that oxygen may have been produced by cyanobacteria along coastal margins of late Archean continents, exemplified by the Gamohaan formation of the Griqualand West basin in South Africa, a carbonate platform formed between 2.6-2.5 Ga.[4,5] Yet, emplacement of large igneous provinces (LIP) periodically drowned this carbonate platform with Fe(II)-rich water.[6] Using a steady-state, 1-D, advective-diffusive transport model, we calculate that Fe(II) supplied to late Archean upwelling zones during LIP could have inhibited cyanobacteria oxygen release due to Fe(II) toxicity. Changing ocean circulation patterns, linked to patterns of mafic volcanism, could therefore have modulated the occurrence and extent of Archean "oxygen oases", and hence, the timing of oxygen's rise in the atmosphere, via Fe(II) toxicity.

We will present these results, along with an outlook of how the persistence of Fe(II) through the Proterozoic may have modulated oxygenation of the deep oceans and influenced the trajectory of oxygen-dependent evolution. We will discuss ongoing investigations that strive to establish testable hypotheses for the relationship between Fe(II) and Earth's oxidation in laboratory settings, modern analogues, and the geological record.

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BIF-type sedimentary rock of the 3.49 Ga Dresser Formation (Western Australia).

A planetary driver of environmental, atmospheric and biological change through the Precambrian

Martin J. Van Kranendonk

University of New South Wales, School of Biological, Earth and Environmental Sciences, Australian Centre for Astrobiology, Sydney, Australia; E-mail: m.vankranendonk@unsw.edu.au

Analysis of global geological data shows that rapid changes in the outer shell of our planet (hydrosphere-atmosphere-biosphere) through the Precambrian may be more closely linked to changes driven from the interior (core-mantle) and crust of the planet than previously considered. This analysis confirms the importance of Earth's supercontinent cycle, not only on the degree of crustal recycling rates that arise from the aggregation and dispersal of supercontinents, but also on mantle temperatures, crustal growth rates, and climatic conditions. Thus, Earth can be defined as operating as a two-state system: Hot mantle periods that accompany supercontinent aggregation are characterised by mantle superplume events, increased crustal recycling and warm, reducing climatic conditions; Cool mantle periods during supercontinent rifting are characterised by low rates of crust production and cool, more oxidizing conditions, leading to widespread, occasionally global, glaciations. Life adapted and evolved to these changing conditions driven by the supercontinent cycle.

Five global supercycles are identified since the inception of modern-style plate tectonics and the onset of the supercontinent cycle at ca. 3.2 Ga, each with attendant changes in the hydrosphere-atmosphere-biosphere. The geological record of these cycles is a triad of superposed rock sequences: 1) greenstones; banded iron-formations; glaciogenic deposits. Further changes to the outer shell result from feedbacks between climate, weathering, tectonics, and biological evolution. These changes have all left their mark in the rock record that can be used to develop a chronostratigraphic Precambrian timescale over most of Earth history and help communicate a more complete, more compelling, history of our planet within the geosciences community and to the general public.

3.5 Ga Apex Basalt (Western Australia) with primary calcite precipitates.

Steven A. Benner
Foundation for Applied Molecular Evolution, Gainesville, USA
sbenner@ffame.org

Martin Blumenberg
Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany (present address); Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany
martin.blumenberg@bgr.de

Bastien Bossau
Université Lyon 1, Laboratoire de Biométrie et Biologie Evolutive, Villeurbanne
bastien.boussau@univ-lyon1.fr

Jan-Peter Duda
Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany
jduda@gwdg.de

Hans-Joachim Fritz
Georg-August-University of Göttingen, Courant Research Centre Geobiology, Göttingen, Germany
hansj.fritz@gmail.de

Chaitanya Giri
Max Planck Institute for Solar System Research, Department Planet and Comets, Göttingen, Germany
giri@mps.mpg.de

Manolo Gouy
Université Lyon 1, Laboratoire de Biométrie et Biologie Evolutive, Villeurbanne
manolo.gouy@univ-lyon1.fr

Mathieu Groussin
Université Lyon 1, Laboratoire de Biométrie et Biologie Evolutive, Villeurbanne
mathieu.groussin@univ-lyon1.fr

Maximilian Halama
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
maximilian.halama@uni-tuebingen.de

Christian Hallmann
Max-Planck-Institute for Biogeochemistry, Organic Paleobiogeochemistry Group, Jena, Germany; University of Bremen, Center for Marine and Environmental Sciences (MARUM), Bremen, Germany
challman@bgc-jena.mpg.de

Bent Hansen
Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany
bhansen@gwdg.de

S. Blair Hedges
Temple University, Center for Biodiversity, Philadelphia, USA
sbh@temple.edu

Daniel Herwartz
University of Köln, Institute for Geology and Mineralogy, Köln, Germany
d.herwartz@uni-koeln.de

Michael Hoppert
Georg-August-University of Göttingen, Institute of Microbiology and Genetics, Department of General Microbiology, Göttingen, Germany
mhopper@gwdg.de

Danny Ionescu
Leibniz Institute for Freshwater Ecology and Inland Fisheries, Department of Experimental Limnology, Stechlin, Germany (present address); Max-Planck-Institute for Marine Microbiology, Department of Biogeochemistry, Bremen, Germany
ionescu@igb-berlin.de

Andreas Kappler
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
andreas.kappler@uni-tuebingen.de

Kurt Konhauser
University of Alberta, Department of Earth & Atmospheric Sciences, Edmonton, Canada
kurtk@ualberta.ca

Wilfried Kramer;
University of Göttingen, Institute of Microbiology and Genetics, Abteilung Molekulare Genetik, Grisebachstr. 8, D 37077 Göttingen
wkramer@gwdg.de

Tom McCollom
University of Colorado Boulder, Laboratory for Atmospheric and Space Physics, Boulder, USA
tom.mccollom@lasp.colorado.edu

Dominik Mühlen
Georg-August-University of Göttingen, Institute of Microbiology and Genetics, Department of General Microbiology, Göttingen, Germany
dominik.muehlen@stud.uni-goettingen.de

Addresses of contributors

Martin Obst
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
martin.obst@uni-tuebingen.de

Andreas Pack
Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany
apack@gwdg.de

Aude Picard
Harvard University, Department of Organismic and Evolutionary Biology, Cambridge, USA (present address);
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
aude.picard@uni.tuebingen.de

Luca Quaroni
ETH Zurich & University of Zurich, Functional Genomics Center Zurich, Zurich, Switzerland (present address);
Paul Scherrer Institute, Infrared Group, Villigen, Switzerland
quaroni@bluewin.ch

Joachim Reitner
Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany
jreitne@gwdg.de

François Robert
Muséum National d'Histoire Naturelle, Paris, France
robert@mnhn.fr

Nadine Schäfer
Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany
nschaef1@gwdg.de

Bettina E. Schirrmeister
University of Bristol, School of Earth Sciences, Bristol, United Kingdom
bettina.schirrmeister@bristol.ac.uk

Gregor Schmid
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
gregor.schmid@uni-tuebingen.de

Sukanya Sengupta
Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany
ssengup@gwdg.de

Zachary Sharp
University of New Mexico, Department of Earth and Planetary Sciences, Albuquerque, USA
zsharp@unm.edu

Andrew Steele
Carnegie Institution of Washington, Geophysical Laboratory, Washington D.C., USA
asteele@carnegiescience.edu

Elizabeth Swanner
Eberhard Karls University of Tübingen, Center for Applied Geosciences, Geomicrobiology, Tübingen, Germany
elizabeth.swanner@ifg.uni-tuebingen.de

Volker Thiel
Georg-August-University of Göttingen, Geoscience Centre, Department of Geobiology, Göttingen, Germany
vthiel@gwdg.de

Martin J. Van Kranendonk
University of New South Wales, School of Biological, Earth and Environmental Sciences, Australian Centre for Astrobiology, Sydney, Australia
m.vankranendonk@unsw.edu.au

Franziska Wilsky
Georg-August-University of Göttingen, Geoscience Centre, Department of Isotope Geology, Göttingen, Germany
fwilsky@gwdg.de

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Herausgeber: J. Reitner, H.-J. Fritz & J.-P. Duda (Göttingen)
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E-mail: jreitne@gwdg.de

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