SPP1833

Building a Habitable Earth

Abstracts

of the Fifth General Meeting

“Early Earth evolution”

March 23-24, 2021

online

Tuesday, March 23th, Morning Session: Evolution of the early solar system and planets

Zoom-Link: https://uni-koeln.zoom.us/j/99864184863?pwd=czlXM1ZGR0RXQ2o0dlRDYjhYclF5QT09
Meeting-ID: 998 6418 4863
Passwort: 155928

9.00-9.20	Carsten Münker, Köln: Introductory remarks and update on SPP activities
9.20-9.40	Dmitry Semenov, Heidelberg: Towards making habitable Earths: the importance of pre-natal physical and chemical conditions
9.40-10.00	Janos Kodolányi, Mainz: No evidence for high ^{60}Fe/^{56}Fe in ancient chondrules
10.00-10.20	Jan Leitner, Mainz: A study of silicon and chromium nitrides in chondritic meteorites: Windows to early solar nebula processes?
10.20-10.50	*Coffee Break (Breakout-Rooms for individual discussions and meetings open)*
10.50-11.10	Frank Wombacher, Köln: Volatile element abundances in Apollo samples determined by isotope dilution ICP-MS
11.10-11.30	Wafa Abouchami, Köln: High precision cadmium stable isotopes in lunar regolith samples
11.30-11.50	Mario Fischer-Gödde, Köln: Ruthenium isotope constraints on the nature of Earth’s late-stage building blocks
11.50-12.10	Ludmila Carone, Heidelberg: Towards a self-consistent multi-outgassing scheme for a magma ocean on the early Earth
12.10-12.30	Sara Vulpius, Berlin: The effect of fractional crystallization on the volatile release from intrusive bodies on early Earth
12.30-13.30	Lunch Break (Breakout-Rooms for individual discussions and meetings open)

Tuesday, March 23th, Afternoon Session: Archean Processes

Zoom-Link: https://uni-koeln.zoom.us/j/93793369521?pwd=cmFGay95WFAwMGJuUExFQVU4Yk0vQT09
Meeting-ID: 937 9336 9521
Passwort: 249050

13.30-14.00	Axel Hofmann, Johannesburg: KEYNOTE
14.00-14.20	René Heller, Göttingen: Habitability of early Earth: Liquid water under a faint young Sun facilitated by tidal heating due to a closer Moon
14.20-14.40	Andrea Piccolo, Mainz: Emergence of plate tectonic during the Archean: insights from 3D numerical modelling
14.40-15.00	Nils Messling, Göttingen: ^{182}W variations in Paleo-Archean mafic and felsic rocks from the Barberton Greenstone Belt, South Africa
15.00-15.30	*Coffee Break (Breakout-Rooms for individual discussions and meetings open)*
15.30-15.50	Jonas Tusch, Köln: Recycled roots of Hadean protocrust – A possible OIB endmember?
15.50-16.10	Lanita Gutieva, Bochum: Comparison of zircon trace element, Lu–Hf and U–Pb record from different parts of the Archean Lewisian Gneiss Complex, NW Scotland
16.10-16.30	Jonathan Lewis, Berlin: Eoarchean TTGs from the Itsaq Gneiss Complex, SW Greenland host recycled, surface derived sulfur
16.30-16.50	Christoph Heubeck, Jena: Detrital zircon provenance of the Archean Moodies Group, Barberton Greenstone Belt, South Africa and Eswatini
16.50-17.10	Deon Janse van Rensburg, Jena: Did volcanism in Moodies estuaries (Barberton Greenstone Belt, 3.22 Ga) assist early microbial life?
17.10-17.30	Sebastian Reimann, Jena: Syndepositional hydrothermalism selectively preserves records of one of the earliest benthic ecosystems, Moodies Group (3.22 Ga), Barberton Greenstone Belt, South Africa
17.30-18.00	Panel discussion
18.00	*optional: Breakout-Rooms for individual discussions and meetings open*

SPP1833
Building a
Habitable Earth

PROGRAMME
General Meeting 2021 – Online
SPP 1833 “Building a Habitable Earth”

Wednesday, March 24th, Morning Session: Origin and early evolution of Life

Zoom-Link: https://uni-koeln.zoom.us/j/95393630681?pwd=VjZQd2FBYXloeGExSCtaaHRQdFFZQT09
Meeting-ID: 953 9363 0681
Passwort: 668199

9.00-9.30	Martin van Kranendonk, Sydney: KEYNOTE
9.30-9.50	Winfried Schwarz, Heidelberg: Biogenic Carbon in Magmatic Minerals and Implications for the Preservation and Obliteration of Hadean Isotopic Biosignatures
9.50-10.10	Florian Kurzweil, Köln: Redox control on the seawater tungsten isotope composition
10.10-10.30	Lucile Roue, Tübingen: Stable W and Mo isotopic data support increasing redox potentials of the Archean ocean through time
10.30-10.50	*Coffee break (Breakout-Rooms for individual discussions and meetings open)*
10.50-11.10	David Ernst, Bremen: The origin of banding in BIFs and the antiquity of the super-chondritic Y/Ho ratio and the lanthanide tetrad effect in seawater
11.10-11.30	Julius Havsteen, Tübingen: The conundrum of correlating the Duitschland and Rooihoogte formation(s) and its consequences for interpreting atmospheric oxygen evolution across the Great Oxidation Event
11.30-11.50	Achim Herrmann, Kaiserslautern: Surviving the ferruginous Archean ocean – Diurnal Fe(II)/(III) cycling in an simulated marine oxygen oasis
11.50-12.10	Sadia Tamanna, Kaiserslautern: How did Cyanobacteria survive increased atmospheric O2 levels during the Great Oxygenation Event? The role of Superoxide Dismutases (SOD).
12.10-13.10	*Lunch Break (Breakout-Rooms for individual discussions and meetings open)*
13.10-13.30	Allison Enright, New Brunswick: Surviving Archean UV-Fluxes: The Role of Iron-Silicate Colloids in attenuating UV for Early Microbial Life
13.30-13.50	Muammar Mansor, Tübingen: Pyrite formation in microbial mats: Linking the present to the past
13.50-14.10	Caroline Unruh, Hannover: Searching for an inorganic signature of life in modern microbial mats
14.10-14.30	Raul Martinez, Bremen: Fraction-specific adsorption of cyanobacterial dissolved organic matter by/on iron (III) oxyhydroxides

Wednesday, March 24th, Afternoon Session: Early Oceans

Zoom-Link: https://uni-koeln.zoom.us/j/94910263795?pwd=MldVSkJvUG5XVnFsVjc4cXVML0lvZz09
Meeting-ID: 949 1026 3795
Passwort: 926913

15.00-15.20	Wanli Xiang, Göttingen: Paleoarchean carbonates – important archives for early Earth’s environments
15.20-15.40	Jakob Surma, Göttingen: Triple oxygen isotopes systematics and clumped isotopes of carbonates – a combined approach using high-resolution isotope ratio mass spectrometry to understand early Earth’s sediment record
15.40-16.00	Oliver Jäger, Göttingen: Tracing the oxygen isotope record of early Precambrian oceans – Insights from oxygen fragment ion analysis and CO_2-O_2 equilibration of carbonates
16.00-16.20	Ashley Martin, Hannover: Uranium and molybdenum records in modern microbial carbonates: an overview
16.20-16.50	*Coffee break (Breakout-Rooms for individual discussions and meetings open)*
16.50-17.10	Helge Mißbach, Köln: Ingredients for early life? Volatile organic compounds in 3.5 Ga old fluid inclusions
17.10-17.30	Eric Runge, Göttingen: A tsunami deposit in the ca. 3.48 Ga Dresser Formation (Pilbara Craton, Western Australia) – Implications for early Archean sedimentary processes
17.30-17.50	Joachim Reitner, Göttingen: Remnants of anaerobic phototrophic benthic mats in the 3.46 Ga Marble Bar Chert Unit (Pilbara, Western Australia)
17.50-18.00	*Concluding remarks*

All abstracts are given in alphabetical order of the first author

High precision cadmium stable isotopes in lunar regolith samples

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Mass-dependent stable isotope fractionation of moderately volatile elements in lunar rocks provide contrasting views on the origin, timing and processes that led to the formation of the Moon. While the “giant impact” between the proto-Earth and Theia provides a framework for the greater volatile element depletion of the Moon relative to the Earth, the mechanisms of volatile loss remain unclear [1]. Here, cadmium isotopes provide important constraints on evaporation/condensation processes. In addition, thermal neutron capture ^{113}Cd (n, γ) ^{114}Cd effects allow estimating the residence time of Cd in the upper layers of the lunar regolith.

We present TIMS double spike Cd stable isotope measurements on five Apollo samples, with an up to 20-fold improvement in analytical precision compared to previous data [2, 3, 4]. In order to distinguish silicate-hosted versus vapor-transport related Cd isotope signals in the regolith, leaching experiments were performed on Apollo 17 orange glass soil 74220 and Apollo 16 mature highlands soil 60500.

Our first results show large stable Cd isotope fractionation of up to ~5‰ amu^{-1}, substantially greater than those of terrestrial and carbonaceous chondrite samples measured alongside the lunar samples. Our data, along those published, demonstrate that Cd stable isotopes, Cd abundances and **n**-capture effects correlate with the soil maturity index (*Is/FeO***)**. These trends suggest progressive Cd depletion with loss of the lighter Cd isotopes during micrometeorite impacts and efficient impact gardening of the lunar regolith. By contrast, the orange glass soil displays a distinctive light Cd isotope signature – similar to that of the leachate – most likely acquired from condensation onto glass bead surfaces of a Cd-rich vapor released during volcanic fire fountaining.

Additional data on the approved lunar samples will be crucial for refining these initial results regarding the origin and processes that defined the Moon’s volatile and isotopic fingerprint and understanding the dynamics occurring at the lunar surface.

[1] Day et al. (2020) EPSL 531, 115998.
[2] Sands et al. (2001) EPSL 186, 103–111.
[3] Schediwy et al. (2006) EPSL 243, 326–335.
[4] Wombacher et al. (2008) GCA 72, 646–667.

Towards a self-consistent multi-outgassing scheme for a magma ocean on the early Earth

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We have recently established a versatile 1D magma ocean model MagmOc [1] in the open source framework VPLANET[1] [2], which is suitable to explore atmospheric outgassing and erosion for the early Earth. Here we couple a thermal evolution model of the interior with an atmosphere including atmosphere erosion. This model so far assumes a pure water vapour atmosphere, which is thought to be the dominant volatile species – provided the early Earth mantle was oxidized. We are currently developing the outgassing scheme further to allow for fully self-consistent outgassing of H_2O and CO_2 and further along the line also other gases such as H_2 and CO. Thus we will be able to explore in more detail how the early magma ocean evolved depending on different mantle redox states as outlined by [3,4]. This line of research is needed to understand the evolution of the total water budget and thus the habitability of early Earth, since it is assumed that in today's Earth 2 – 10 terrestrial oceans are present and have been present since at least the end of the last magma ocean stage – after the Moon impact event [5].

[1] Barth, P. et al. (in press) Astrobiology
[2} Barnes, R. et al. (2020), Publications of the Astronomical Society of the Pacific, Volume 132, Issue 1008, id. 024502 (2020). 61 pp.
[3] Ortenzi, G. et al. (2020) Scientific Reports, Volume 10, article id. 10907
[4] Guimond et al. (in review) Physics of the Earth and Planetary Interiors, revised and resubmitted
[5] Hosono,N. et al. 2019, Nature Geoscience, Volume 12, Issue 6, p.418-423

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[1] https://github.com/VirtualPlanetaryLaboratory/vplanet

Surviving Archean UV-Fluxes: The Role of Iron-Silicate Colloids in Attenuating UV for Early Microbial Life

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During the Archean, Earth's surface was subjected to UV radiation levels 10-1000 times greater than current. Radiation wavelengths from 200-300 nm are known to kill cells within minutes of exposure. It has been demonstrated that silicate and Fe(III) (oxyhydr)oxide mineral phases[1,2,] as well as Si-Fe-aggregates[3], can attenuate UV radiation, allowing cells to survive. Unlike the other phases, Si-Fe colloids are translucent, allowing visible wavelengths to pass through while attenuating damaging UV wavelengths. This property is particularly relevant to phototrophic microbes which depend on photosynthetically active radiation (PAR) as an energy source, but must withstand the stress of UV exposure. The role of such minerals, which are thought to be precursor mineral phases to banded iron formations (BIF), in microbial survivability of UV stress has been investigated here. We exposed cultures of cyanobacteria and Fe(II)-oxidizing marine phototrophs (photoferrotrophs) to UV light for 10 and 20 minutes, then inoculated the exposed cultures into sterile media for most probable number (MPN) analysis of the concentration of viable cells surviving the UV exposure.

Table 1: MPN results of post-UV exposure cultures. Four conditions were tested: UVP, UV-exposed with particles; UVNP, UV-exposed without particles; NUVP, not exposed to UV with particles; and NUVNP, not exposed to UV and without particles. Not UV-exposed cultures were inoculated like the exposed cultures, then wrapped in foil. Exposures were done in an anoxic glovebox with N_2 *atmosphere, 8W 254 nm water purification lamp, at a distance of 25 cm, and exposure depth of 1 cm. MPN estimates based on 9 replicates per condition. Photoferrotrophs were incubated for 10 weeks, cyanobacteria for 6 weeks.*

Strain	Exposure time	UVP	UVNP	NUVP	NUVNP	UVP / UVNP	UVP / NUVP
Rhodovulum iodosum	10 min	2.45×10^4	8.55×10^2	2.68×10^4	8.84×10^5	28.7	0.916
	20 min	3.95×10^4	1.50×10^3	3.84×10^4	4.61×10^3	26.4	1.029
PCC7002 *Synechococcus sp.*	10 min	3.73×10^2	0.00	2.12×10^3	4.16×10^1	--	0.176
	20 min	4.61×10^2	0.00	4.77×10^2	7.63×10^1	--	0.965
PCC7376 *Leptolyngbya sp.*	10 min	1.64×10^2	0.00	3.87×10^1	1.09×10^1	--	4.23
	20 min	4.25×10^1	0.00	1.94×10^1	0.00	--	2.19

There was a consistent trend across all three microbial strains that the presence of Fe-silicate colloids dramatically increased the survivability of prolonged UV exposure. Subsequent batch culturing experiments in the presence and absence of the Fe-silicate particles revealed no negative effects on the growing cells due to the presence of the colloids. It appears that colloidal particles may have played a critical role in helping microbes survive the extreme UV-stress of the Archean ocean environment.

[1] Gauger, T. et al. Geology G37095.1 (2015).
[2] Gauger, T. et al., Astrobiology 16, 301-310 (2016).
[3] Mloszewska, A.M. et al. Nat Commun 9, 3088 (2018).

The origin of banding in BIFs and the antiquity of the super-chondritic Y/Ho ratio and the lanthanide tetrad effect in seawater

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For more than a century, the origin of the enigmatic banding of BIFs is a matter of controversial debate. While some argue for a primary origin reflecting precipitation of Fe-dominated and Si-dominated bands, respectively, from different water masses, others favour a secondary origin and argue for diagenetic separation of the bands from an initially homogeneous Fe-Si precipitate. To address this issue, we investigated the millimetre-scale variation of the REY distribution in BIFs using micro drill cores from adjacent magnetite/haematite and metachert bands from the 2.5 Ga old Mt Ruker BIF from the Prince Charles Mts in East Antarctica.

High sample purity is revealed by low concentrations of Al, Zr, Hf, and Sc. The Mt Ruker BIF is a typical Algoma-type BIF whose chemical composition matches closely that of other early Precambrian BIFs, except for an enrichment of Ni, and elevated Ba/Sr ratios in the metachert. Shale-normalized (SN) REY patterns show all the features of modern seawater such as depletion of light vs heavy REYSN, positive anomalies of LaSN, GdSN, and YSN, but positive EuSN and no CeSN anomalies (and no positive Eu anomalies in chondrite-normalized REY patterns). This distribution is fully compatible with that of other pure Early Precambrian BIF, suggesting high-temperature hydrothermal input of REY into seawater and a redox level of the atmosphere-hydrosphere system too reducing for Ce oxidation. Besides super-chondritic Y/Ho ratios, both the metachert and the Fe-oxide bands show the W-type lanthanide tetrad effect (LTE). This agrees with observations in other BIFs including the oldest one at Isua, Greenland, and hence reveals the antiquity of these phenomena. This corroborates that W-type LTE and positive Y anomalies (the latter possibly of smaller size than today) have always been characteristic features of seawater and did not change significantly over the almost 4 billion years long geological record of seawater composition. They are, however, in marked contrast to the REY distribution in Modern and Cenozoic oxidic hydrogenetic ferromanganese crusts, pointing towards a fundamentally different removal mechanism of REY from Modern vs Early Precambrian seawater.

We emphasize that adjacent iron-oxide and metachert BIF bands both show uniform super-chondritic Y/Ho ratios and the W-type LTE, similar to those observed in marine sedimentary carbonates, i.e. there is only very minor REY fractionation between the precipitate and ambient seawater. This is not only at odds with results from scavenging and sorption experiments that investigated REY partitioning between Fe and/or Mn (oxyhydr)oxides and aqueous fluids, but also with observations at marine and terrestrial natural systems, where the Fe (oxyhydr)oxides show sub-chondritic Y/Ho ratios and the M-type LTE in spite of having formed from solutions with super-chondritic Y/Ho ratio and W-type LTE. If the initial BIF precipitate had been a homogenous Fe-silicate, any later separation and redistribution of Fe and Si would have resulted in different Y/Ho ratios and LTE orientation in adjacent Fe oxide and chert bands. This, however, is not observed. The millimeterscale REY distribution across BIF bands, therefore, strongly suggests that the conspicuous banding of BIFs is of primary origin and does not result from post-depositional separation of an initially homogenous Fe-Si precipitate.

Ruthenium isotope constraints on the nature of Earth's late-stage building blocks

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Ruthenium belongs to the group of highly siderophile elements (HSE:Re-Os-Ir-Ru-Rh-Pt-Pd-Au), which are key elements for studying core formation and late-stage accretion processes on Earth and other planetary bodies. Owing to their iron loving character, it would be expected that HSE would be almost quantitatively extracted to the core during metal-silicate differentiation. Hence, Ru and other HSE abundances in the mantle today are interpreted to derive from late accretion of a 'late veneer' consisting of meteoritic materials that were added to the Earth after core formation had ceased.
However, experimental studies revealed that the tendency of some HSE to bond with iron decreases significantly under high pressure and temperature conditions of core formation and that it would also be feasible to, at least partially, explain the mantle composition by incomplete extraction of HSE during late-stage core formation processes [1]. Thus, the Ru isotope inventory of the modern mantle may consist of a mixture of two different fractions: one deriving from the late veneer and the other fraction predating the late veneer. The pre-late veneer fraction has been identified in Archean mantle-derived rocks from SW Greenland (3.8-3.0 Ga) and komatiites from the Pilbara (3.5-3.2 Ga) and Yilgarn (2.7 Ga) cratons as it is distinct from the composition of the modern mantle (by +20 ppm) [2,3]. The presence of such pre-late veneer Ru on Earth opens a unique new perspective not only for assessing the nature of Earth's building blocks towards the end of its main accretion and before modification of the mantle composition by the late veneer, but also for constraining the nature and origin of the late veneer material.
The preserved Ru isotope vestige of the pre-late veneer mantle is best explained by late mixing of carbonaceous chondrite-like late veneer fraction into Earth's mantle [3]. Towards the end of the Archean eon, the transition from a stagnant lid mode to a plate tectonic regime with deep reaching subduction caused efficient mixing of the late veneer component, resulting in a homogeneous modern mantle composition.

[1] Rubie et al. (2016) Science.
[2] Fischer-Gödde et al. (2020) Nature.
[3] Fischer-Gödde et al. (2020) Goldschmidt.

Comparison of zircon trace element, Lu–Hf and U–Pb record from different parts of the Archean Lewisian Gneiss Complex, NW Scotland

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The Lewisian Gneiss Complex (LGC) is a portion of Archean basement that is traditionally divided into a northern, central, and southern region based on structural, geochemical, and geochronological data. It is currently unclear whether the complex consists of several distinct terranes or if it represents a continuous fragment of Archean crust. Here we present the results of U-Pb, trace element and Lu–Hf analysis on zircon cores, and U–Pb data from zircon rims in combination with sample petrography and zircon cathodoluminescence (CL) from twenty tonalite-trondhjemite-granodiorite (TTG) gneiss and seven granitic gneiss samples. Zircon cores from TTG gneisses exhibit igneous oscillatory zoning and enrichment in HREE, indicating their magmatic origin and partial melting in the absence of garnet. In the central region, zircon cores show negative Eu anomalies, indicating plagioclase fractionation prior to zircon crystallisation, or that plagioclase remained in the source. In TTG gneisses from the southern and northern regions zircon cores show overall higher abundances of REE, especially LREE and MREE, and lack distinct Eu anomaly.

In all three regions, the variations of the Hf isotopic values in zircon cores (mean εHf_i = +2.5 to -1.2) reflect a magma source that was derived from a mixture of juvenile and reworked crustal material. Exceptions are recorded for a central region tonalitic gneiss ($\varepsilon Hf_{2.97\ Ga}$ = +4.5), and two granitic gneisses ($\varepsilon Hf_{2.69Ga}$ = –1.5 and –2.5), which suggest a juvenile and a reworked crustal source, respectively. Zircon U–Pb analyses from the central region samples define a continuous and overlapping spread of apparent core and rim ages, suggesting variable extents of metamorphic recrystallization. Oldest concordant zircon core ages in individual samples from the central region span between 2.76 Ga and 3.0 Ga and are interpreted as protolith ages. CL-bright zircon rims record a smear of ages from ca. 2.8 to 2.4 Ga that overlap with a similar smear of ages in the zircon cores, suggesting a protracted period of high-ultrahigh temperature conditions for >0.2 Ga. The crystallization ages in the northern and southern regions, estimated from the upper-intercept ages, range between 2.82 and 2.63 Ga and 3.11–2.63 Ga, respectively. These samples also lack the typical 'smear' of zircon ages observed in the central region, indicating that a prolonged granulite facies metamorphic event was not recorded in the southern and northern region zircons. A range of εHf_i values around chondritic signatures within individual samples suggests incorporation of both older crustal and more juvenile material. At present, our data show that the formation of TTG gneisses in all three regions involved comparable processes and sources, and was broadly coeval, albeit the subsequent tectono-thermal evolution of the three regions appears to have been different.

The conundrum of correlating the Duitschland and Rooihoogte formation(s) and its consequences for interpreting atmospheric oxygen evolution across the Great Oxidation Event

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The stratigraphic relationship between the Duitschland formation and the Rooihoogte formation in the Transvaal Basin (South Africa) is still not settled. Some authors argue that the Duitschland and Rooihoogte formations are coeval in time and simply represent the same formation at different proximity to the paleoshoreline [1, 2, 3]. Others prefer to see them as two distinct entities [4, 5]. The correlation between the two formations becomes critically important when viewed in the light of the Great Oxidation Event (GOE), because both formations record the transition from mass-independent to mass-dependent fractionation of sulfur isotopes. A time equivalent deposition of the formations points towards the GOE being an irreversible event. On the contrary, a decoupling of the two formations indicates that the atmospheric oxygen evolution across the GOE was an oscillating and dynamic process. Based on lithological, sequence stratigraphic and geochemical similarities, this work tries to correlate four drill cores from the CIMERA-Agouron GOE Drilling project intersecting both the Duitschland and the Rooihoogte formations. Our data show that the drill cores have the same provenance and thus might be viewed as one formation. In addition, geochemical discrimination diagrams coupled with zircon ages from the Duitschland formation by [6] suggest that the main source area must be a felsic igneous complex with an age of 2410-2575 Ma.

[1] Coetzee, L (2001) PhD thesis, University of Johannesburg.
[2] Hoffman, P.F (2013) Chemical Geology 362, 143-156.
[3] Luo, G et al. (2016). Science Advances 2.5.
[4] Gumsley, A et al. (2017) Proceedings of the National Academy of Sciences 114, 1811-1816.
[5] Moore, J.M et al. (2012) Journal of African Earth Sciences 64, 9-19.
[6] Schröder, S et al. (2016) Precambrian Research 278, 362-393.

Habitability of early Earth: Liquid water under a faint young Sun facilitated by tidal heating due to a closer Moon

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Geological evidence suggests liquid water on the earth's surface as early as 4.4 gigayears ago [1,2] when the faint young Sun only radiated about 70 % of its modern power output. At this point, Earth should have been a global snowball if it possessed atmospheric properties similar to those of modern Earth [3]. An extreme atmospheric greenhouse effect [4], an initially more massive Sun [5], release of heat acquired during the accretion process of protoplanetary material, and radioactivity of early Earth material have been proposed as reservoirs or traps for heat. For now, the faint-young-sun paradox persists as an important problem in our understanding of the origin of life on Earth. We explored the possibility that the new-born Moon, which formed about 69 million years (Myr) after the ignition of the Sun, generated extreme tidal friction – and therefore heat – in the Hadean and possibly the Archean earth. We show that the Earth-Moon system has lost about 3×10^{31} J (99 % of its initial mechanical energy budget) as tidal heat [6]. Tidal heating of about 10 Wm^{-2} through the surface on a time scale of 100 Myr could have accounted for a temperature increase of up to 5°C on early Earth. Tidal heating alone does not solve the faint-young-sun paradox but it could have played a key role in combination with other effects [6]. Future studies of the interplay of tidal heating, the evolution of the solar power output, and the atmospheric (greenhouse) effects on early Earth could help in solving the faint-young-sun paradox, particularly if tied to geologic evidence.

[1] Sagan, C. and Mullen, G. (1972) Science, 177, 52–56
[2] Mojzsis, S. J et al. (2001) Nature, 409, 178–181
[3] Wilde, S. A. (2001) Nature, 409, 175–178
[4] Kuhn, W. R. and Kasting, J. F. (1983) Nature, 301, 53–55
[5] Whitmire, D.P. et al. (1995) J Geophys Res, 100, 5457–5464
[6] Heller, R. et al. (2021) submitted for peer review. pre-print: https://arxiv.org/abs/2007.03423

Surviving the ferruginous Archean ocean – Diurnal Fe(II)/(III) cycling in an simulated marine oxygen oasis

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The oxygenation of early Earth's atmosphere during the Great Oxygenation Event, is generally accepted to have been caused by oceanic Cyanobacterial oxygenic photosynthesis. Some studies suggest that Fe(II) toxicity may have delayed the Cyanobacterial expansion in the ferruginous Archean ocean necessary for the GOE. However, studies with different growth systems found conflicting results for the extent of Fe(II) toxicity and its oxidation. This study re-evaluates the findings as presented in the literature. By using species from the basal clade of Cyanobacteria, we compare the influence of different growth systems commonly used to simulate an Archean environment. Additionally, the toxicity of repeated Fe(II) exposure, in a simulated tidal environment, and the effect of green rust is assessed for *Pseudanabaena* sp. PCC7367. *Pseudanabaena* sp. PCC7367 and *Synechococcus* sp. PCC7336, were incubated under an anoxic, elevated CO_2 atmosphere in buffered ASNIII media with increasing Fe(II) concentrations (15 µM, 120 µM & 600 µM). CO_2 concentrations were either 10% in closed bottles or a regulated atmosphere of 0,2% CO_2 in an anoxic workstation. The Fe(II) toxicity response in the closed bottle cultures could be replicated as presented in the literature. However, this toxicity was not observed in cultures provided with continuous gaseous exchange that showed significantly shorter doubling times than the closed-culture system, even with repeated nocturnal addition of Fe(II) for 12 days. The green rust formation observed in the open system at high Fe(II) concentrations, appeared to have a strong inhibitory effect on Cyanobacterial growth. In contrast the direct addition of green rust was not found to be toxic to *Pseudanabaena* sp. PCC7367. Also, O_2 measurement in the anoxic growth systems exhibited an increased net O_2 production rate under anoxic conditions when compared to cultures grown under an atmosphere with present O_2 levels.

Concluding from this it is possible that Fe(II) in the Archean ocean may have prevented the migration of Cyanobacteria in the open ocean by the formation of green rust, while having no to little effect on the colonisation of shallow water environments, where the localised oxygenic photosynthesis would have created oxygen oases.

Detrital zircon provenance of the Archean Moodies Group, Barberton Greenstone Belt, South Africa and Eswatini

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Sandstones of the 3.22 Ga Archean Moodies Group represent one of the world’s oldest quartz-rich sedimentary sequences. The provenance of this unit is unresolved because its quartz and common microcline can be sourced either from hypothetical, now eroded or covered granitoid plutons outside the Barberton Greenstone Belt (BGB) or, perhaps more controversially, from (rhyo-)dacitic (sub-)volcanic rocks within the BGB.

We compiled 31 detrital zircon data sets (n=2588) from sandstones, reworked tuffs and conglomerate of the Moodies Group in order to constrain its age-provenance. After selecting for quality criteria, remaining zircons (n=1623) in nearly all samples show a distribution corresponding to the four known major pulses of felsic magmatism in the BGB: 1) ca. 3550-3530 Ma (Theespruit and Sandspruit Formations at the base of the Onverwacht Group); 2) ca. 3440-3410 Ma ((rhyo-)dacites of the upper Hooggenoeg Formation, Onverwacht Group); 3) ca. 3300-3280 Ma (thin felsic tuffs in the Mendon Formation); and 4) ca. 3260-3215 Ma (felsic volcanic and shallow intrusive rocks of the upper Fig Tree Group, of the Moodies Group, and their co-magmatic plutonic counterparts. Almost all data sets also contain near-concordant younger zircons (as young as 2820 Ma), which can be attributed to one of six tectonic or magmatic events affecting the young Kaapvaal craton in post-BGB time, causing the partial or complete reset of the U-Pb system in some grains. The youngest (near-)concordant zircon clusters yield ages of ca. 3220 Ma in most locations. The youngest discordant group of zircons from a reworked tuff near the top of the Moodies Group at 3209±14 Ma agrees well with previous estimates of the maximum depositional age. With very few exceptions, the oldest zircons (ca. 3564 Ma) are only slightly older than the oldest rocks in the BGB stratigraphy (ca. 3550 Ma). Subtle regional and stratigraphic differences in age spectra may indicate localized or nearby sediment sources within a synorogenic setting. Preliminary age spectra along vertical stratigraphic profiles show little systematic variation, possibly indicating that intrabasinal recycling was important during the basin’s evolution although extrabasinal plutonic sources, providing quartz and some feldspar, cannot be excluded. All zircon age spectra, limited zircon Hf isotope data, sandstone petrography, facies analysis, and the high variability in Moodies conglomerate clast composition are consistent with uplift, deformation and erosion of intra-BGB sources, in particular the region of the Onverwacht Anticline. Zircon populations, conglomerate clasts, and sandstone composition show no positive evidence that high-grade metamorphic rocks from the adjacent Ancient Gneiss Complex (AGC) contributed significantly to the Moodies Group.

Tracing the oxygen isotope record of early Precambrian oceans – Insights from oxygen fragment ion analysis and CO2-O2 equilibration of carbonates

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The oxygen isotope record of carbonates displays a systematic rise in $\delta^{18}O$ of 10 to 15‰ from the Archean towards the Phanerozoic. Three scenarios are suggested to account for this isotopic shift: (I) hot Archean oceans, (II) an early ocean, that is depleted in ^{18}O compared to present day and (III) post-depositional alteration [1]. Here we present triple oxygen isotope data of ancient platform carbonates from the Campbellrand and Mooidrai formation from the Kapvaal craton, South Africa to decipher the oxygen isotope conundrum of the Late Neoarchean to Early Paleoproterozoic oceans. We measured the triple oxygen isotope composition of CO_2 generated by phosphoric acid digestion of carbonates with the Thermo Scientific Ultra high-resolution isotope ratio mass spectrometer (HR-IRMS) by the oxygen ion fragment method [2]. All carbonate samples plot below a recently predicted equilibrium curve between present day seawater and carbonate and do not reflect a pristine oxygen isotope signature. The data do not support hot ocean temperatures at the Archean-Proterozoic boundary, that were significantly higher than today and no oceans with lower $\delta^{18}O$ of seawater. Modelling of diagenetic alteration suggests that the primary isotopic signature was modified. An alternative scenario that could explain the observed data is, that the carbonates last reequilibrated with (sea)water with slightly higher $\delta^{18}O$ and lower $\Delta'^{17}O$ [3]. To verify and cross-calibrate these results we developed another method to determine the triple oxygen isotope composition of carbonates, that is based on the catalytic isotope exchange between CO_2 and O_2 over a hot platinum-wire [4,5]. We present a modified experimental setup of this method. To minimize potential isotopic exchange with hot glass surface we only heated the platinum-wire to a temperature of 900°C. We developed an automatized procedure to minimize external error sources. We show that full equilibration in $\delta^{18}O$ can be achieved between both gases after 15 min of exchange. By measuring $^{17}O/^{16}O$ and $^{18}O/^{16}O$ of the reacted O_2 and $^{18}O/^{16}O$ of CO_2 before and after the reaction, $\Delta'^{17}O$ in initial sample CO_2 is calculated with a mass balance equation.

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Did volcanism in Moodies estuaries (Barberton Greenstone Belt, 3.22 Ga) assist early microbial life?

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The Moodies Group of the BGB provides a high-resolution window into Archaean sedimentary, magmatic and ecological processes. Its magmatic component, the Moodies Igneous Complex (MIC), has to date been largely overlooked. The MIC consists of several mafic-to-intermediate sills, peperitic dyke stockworks, extensive basaltic lava flows, and various volcaniclastic deposits and tuffs, all of Moodies depositional age. Excellent outcrop exposures illustrate diverse and dynamic interactions between volcanic activities and shallow-water sedimentary processes; they constrain the conditions in which microbial communities thrived in estuarine and tidal environments. (1) When the Moodies lava flooded the Moodies basin, its fragments and pillows were reworked as boulder-sized conglomerate clasts and in gravelly sandstones while still plastic and presumably hot. (2) Aerodynamically-shaped ejecta of mafic lava and common sand-sized tephra shards in cross-bedded sandstones demonstrate explosive lava-water interactions- loading of unconsolidated sands by lava may have produced rootless volcanic cones. (2) Dacitic (lapilli) tuffs up to several m thick were eroded by estuarine channels and filled back-beach lagoons, modifying and smothering concurrent aqueous transport by saltation and as bedload. (3) The paleo-groundwater table and the MIC interacted vigorously by *in-situ* fluidization of poorly to unconsolidated sediment, entrainment of grains and sandstone xenoliths in mafic (sub-)volcanics, widespread peperite formation, and formation of lava-filled fractures and abundant quartz veins in sandstones.

We speculate that the proximity of numerous shallow intrusives, lavas, and volcanic tephra provided Moodies tidal-facies microorganisms with abundant thermal and chemical energy. Heavy mineral lags in the estuaries, combined with potentially aggressive weathering of mafic and ultramafic rock, released ample nutrients (transition metals and P). Drying-and-wetting cycles on tidal flats and coastal plains, the high porosity and permeability of the well-sorted quartzose sediment in shallow water, the variably energetic current regime, and the anoxic, reducing-to-oxidizing chemistry of these habitats also benefitted microbial communities. Moodies Group volcano-sedimentary estuarine environments may have provided an ideal incubation laboratory for early Archean life.

No evidence for high $^{60}Fe/^{56}Fe$ in ancient chondrules

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The abundance of the short-lived radioactive isotope ^{60}Fe ($t_{½}$ = 2.62 ± 0.04 million years; [1]) in the early solar system is relevant for models of planetary differentiation (e.g., [2]). Isotope measurements of bulk samples of early solar system materials indicated that the solar system's $^{60}Fe/^{56}Fe$ ratio at the time of its formation was most likely 1 (± 0.1) × 10^{-8} [3]. However, in situ isotope data, most of which were obtained on chondrules from unequilibrated ordinary chondrites (UOCs), suggested that the ratio might be 1–2 orders of magnitude higher [4,5]. Measurement bias, as well as the effects of aqueous alteration and metamorphic re-equilibration have been suggested as reasons behind the difference between bulk and in situ results [6,7]. Using the NanoSIMS, we have been able to measure the nickel isotope composition and Fe/Ni ratios of chondrule phases (olivine, enstatite, silicate glass, and troilite) at higher spatial resolution, than achieved previously (few µm vs. ≥10 µm), which allowed us to avoid nickel-rich inclusions, and alteration phases. We focussed our efforts on chondrules from UOCs and primitive carbonaceous chondrites. We estimated the age of some of the studied chondrules relative to the canonical calcium- and aluminium-rich inclusions (CCAIs), based on Mg-Al isotope compositions (data also obtained by the NanoSIMS). We have not found evidence for in situ ^{60}Fe decay in any of our chondrules, even though some of them are old enough (minimum age 1.13 +0.23/−0.19 million years after CCAIs), and have large enough Fe/Ni ratios ($^{56}Fe/^{62}Ni$ up to 1.9 million in troilite and 1.6 million in silicates), to produce an enrichment in ^{60}Ni detectable with the NanoSIMS, provided $^{60}Fe/^{56}Fe$ ratios estimated previously for some chondrules based on in situ measurements (~10^{-6}; [4]) are accurate. We measured nickel isotope anomalies consistent with statistical variations assuming ~terrestrial nickel isotope compositions, and with the low initial $^{60}Fe/^{56}Fe$ ratios inferred from previous isotope data on bulk samples: the average $^{60}Fe/^{56}Fe$ inferred for our chondrules is $1.62 \pm 2.77 \times 10^{-8}$ (1σ).

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Redox control on the seawater tungsten isotope composition

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Manganese oxides are a major sink for dissolved marine WO_4^{2-} and MoO_4^{2-}. During adsorption of WO_4^{2-} and MoO_4^{2-} onto Mn oxides the coordination of W and Mo changes from tetrahedral to octahedral [1]. Light isotopes are preferentially adsorbed due to the weaker bonding structure in octahedral coordination. Sulfidic settings are another major sink for Mo, but not for W [2, 3]. In contrast to Mo, the $\delta^{186/184}$W of seawater and authigenic sediments is therefore expected to be independent of the global extension of sulfidic conditions but more intimately linked to the extension of oxic marine conditions.

We present seawater $\delta^{186/184}$W and W concentration data from the South Atlantic Ocean and the South China Sea showing an average $\delta^{186/184}$W of +0.543 ± 0.046 ‰ (2SD; n = 10) at an average W concentration of 0.050 ± 0.007 nM (2SD; n = 10). These estimates are perfectly consistent but more precise than a previous estimate on Northern Pacific seawater [4] and clearly indicate a conservative distribution of W in modern open ocean seawater. In contrast, seawater from a redox-stratified basin in the more restricted Baltic Sea (Landsort Deep) shows more variable W isotope compositions ($\delta^{186/184}$W between +0.347 and +0.810 ‰) and W concentrations (between 0.054 and 0.223 nM). Consistent with experimental studies [1], the preferential scavenging of isotopically light W by Mn oxides that form along the redoxcline in this basin increases the $\delta^{186/184}$W of surrounding seawater, whereas the re-dissolution of Mn oxides causes decreasing seawater $\delta^{186/184}$W. Our findings suggest that redox-related processes cause variations in the abundance and stable isotope composition of marine W thus providing the initial framework for the future application of stable W isotopes as a new paleo-redox proxy.

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A study of silicon and chromium nitrides in chondritic meteorites: Windows to early solar nebula processes?

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Nitrogen is the most abundant component in Earth's atmosphere and one of the key elements for the evolution of Earth's biosphere. However, the types of nitrogen carriers, their abundances and nitrogen isotopic compositions are not well constrained for all potential terrestrial building blocks. Chondritic meteorites contain small quantities of various nitrides. While Si_3N_4, TiN, and sinoite (Si_2N_2O) occur frequently in low abundances in enstatite chondrites (ECs), Si_3N_4 has been reported only on very few occasions in several ordinary chondrites (OCs) [1] and Acfer 182 (CH3) [2]. TiN has only been found in the carbonaceous chondrites Allan Hills (ALH) 85085 (CH3) and Isheyevo (CH/CB) [3–6], and recent studies reported CrN (carlsbergite) in CM chondrites [7,8]. We report the discovery of Si_3N_4 and CrN in several carbonaceous chondrites (CCs). The average N-isotopic compositions of nitrides from CCs and ECs [9] differ significantly, and we also observe variations between different CC groups. Nitrogen becomes isotopically heavier in nitrides from EC-(OC-) through CV&CM to CR-CH&CB chondrites. This may indicate increasing amounts of outer Solar System N in the respective reservoirs of nitrides, and could reflect different heliocentric distances of the formation regions [10]. However, we also observe that the N-isotopic compositions of nitrides are sometimes significantly different from those of their host meteorites and meteorite groups [e.g.,9,11]. This suggests several different N reservoirs and/or different formation/alteration pathways for the various N-carriers within a given meteorite group.

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Eoarchean TTGs from the Itsaq Gneiss Complex, SW Greenland host recycled, surface derived sulfur

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Eoarchean TTGs form the cores of Earth's oldest cratons. Competing hypotheses concerning the geodynamic context of TTG formation in the Eoarchean, including vertical and horizontal tectonic processes, continue to be debated. Constraining the nature of the source rocks that melted to form the TTGs is a crucial part of resolving this debate. The formation of the first continental cratons played a key role in producing the diverse habitats necessary for the evolution of life on Earth. To cast fresh light on this question, we present first multiple sulfur isotope analyses on a well characterized suite of Eoarchean TTGs and associated amphibolites from the 3.6-3.9 Ga Itsaq Gneiss Complex, southern West Greenland. We apply our results to investigate whether surfaced-derived sulfur was incorporated into the source rocks of juvenile TTGs and the mantle sources of potentially genetically related amphibolites. Sulfur isotope analyses were performed by gas source mass spectrometry. Additionally, sulfide textures and chemical compositions were analyzed by electron microprobe. Small but significant nonzero $\Delta^{33}S$ and $\Delta^{36}S$ values were measured in the TTGs, with $\Delta^{33}S$ values from 0.00‰ to +0.30‰, and $\Delta^{36}S$ values from -0.13‰ to +0.80‰. The amphibolites had $\Delta^{33}S$ values of -0.01‰ and +0.14‰, and $\Delta^{36}S$ values of +0.08‰ and +0.23‰. The $\Delta^{33}S$ values of the TTGs support previous studies proposing a genetic link between the TTGs and local amphibolites with tholeiitic composition (e.g. (1, 2)) and reveal that both rock types have incorporated mass-independently fractionated, surface-derived sulfur. The presence of this isotopic signal indicates that crustal recycling mechanisms, possibly similar to modern tectonic processes, were active as early as 3.8 Ga. We also observe isotopic and textural evidence in sulfides for further modification of sulfur isotopes now hosted in the TTGs. This modification followed the sulfur's emplacement in the TTGs' source amphibolites, and may have been related to metamorphic processes taking place during crustal thickening in the Eoarchean.

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Uranium and molybdenum records in modern microbial carbonates: an overview

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Stromatolites were the prevalent forms of biogenic carbonate deposition in the Precambrian and were likely present at least one billion years before the rise of oxygen on Earth during the "Great Oxidation Event" (GOE; ca. 2.4 – 2.3 Ga). Isotopic variations of redox sensitive elements, such as uranium (U) and (Mo), in stromatolitic carbonates from the Archean may reveal the surface oxidation state of the ancient oceans. However, as U and Mo isotopes may be fractionated during stromatolite formation and/or early sedimentary diagenesis, it is of interest to assess variations of U and Mo in modern stromatolites. In this project, we collected modern stromatolites from key sites globally. Component-specific analyses with LA-ICP-MS show that micrite, a key signature for microbial carbonate precipitation, is highly but variably enriched in U relative to Mo in marine stromatolites, e.g., U/Mo ranged from 17 to 64 in micrite from stromatolites from the marine hypersaline Shark Bay, Western Australia. However, in lacustrine stromatolites from volcanic rift zones, e.g., Lake Chew Bahir, Ethiopia, U/Mo of micrite was much lower (0.3 to 2.9). To target the microbial carbonate phases for our U and Mo isotopic investigations, we adopted a selective leaching procedure using acetic acid, which provided similar U/Mo patterns to those measured in micrite by LA-ICP-MS. This selective leaching approach shows that modern marine stromatolite tops from Shark Bay yielded a narrow range of δ^{238}U from -0.30 to -0.33‰, corresponding to an offset of ca. +0.1‰ from seawater, whereas deeper stromatolite laminae exhibited values up to +0.11‰. Such high δ^{238}U in the deeper laminae indicate U isotope fractionation, likely associated with U reduction during early sedimentary diagenesis. In contrast to the marine stromaotlites, the δ^{238}U of lacustrine stromatolites from Lake Chew Bahir, Ethiopia ranged from -0.48 to +0.03‰ and varied with sample morphology, environmental parameters (as recorded by δ^{13}C, δ^{18}O), and Mo concentrations. Our Mo isotopic investigations are still underway as they have been somewhat limited by the low Mo concentrations in marine stromatolites, particularly with larger sample size requirements for a selective leaching approach.

Fraction-specific adsorption of cyanobacterial dissolved organic matter by/on iron (III) oxyhydroxides

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The interaction of cyanobacteria dissolved organic matter with precipitating iron (III) oxyhydroxide phases was investigated. Cyanobacteria have been ubiquitous in aquatic systems for 3.5 Ga, regulating the oxygen levels in the past and present atmosphere, and contributing to the carbon cycle in fresh- and seawater. As such, cyanobacteria generate significant amounts of particulate organic matter (POM), but in addition, they contribute a much less studied dissolved organic matter (DOM) fraction to the total organic carbon pool in freshwater and marine environments. Understanding the modes of interaction of cyanobacteria DOM with abundant mineral phases such as iron (III) oxyhydroxides provides further insight into the mechanisms of organic carbon long term storage and remineralization. In this study, cyanobacteria cultures grown to maximum period of 8 weeks, were investigated for their DOM quality and quantity, and the interaction of cyanobacterial DOM with precipitating iron (III) oxyhydroxide mineral factions. The results of experiments herein, suggest two modes of cyanobacteria DOM interactions with precipitating iron (III) oxyhydroxides. FT-ICR-MS analyses of control samples and those in the presence of iron (III) oxyhydroxides, showed differences in H/C and O/C rations as function of cyanobacteria culture age. With older cultures, with signs of cell lysis and natural cell death, a compositional difference is present between the organic molecular types in supernatant samples and those co-precipitated with iron (III) oxyhydroxide pellets. Overlap of H/C and O/C ratios for cyanobacteria cultures 2 to 6 weeks old, suggest no or little fractionation of the DOM by iron mineral reactive solid. This implies that cell lysis would enhance the presence of organic molecules from within the cyanobacteria cell able to be co-precipitated by the forming iron (III) mineral phase. Further results presented in this study, suggest that a fraction of the cyanobacteria dissolved organic matter can also weakly sorb to the iron (III) reactive solid surface. Elemental analyses of freeze-dried iron (III) oxyhydroxide pellets showed that 2 to 3% of the total cyanobacteria dissolved organic carbon (DOC) is occluded/co-precipitated within iron (III) mineral structures. This result is of significant importance, when extrapolated to the natural environment, for the quantification of the role of reactive iron oxides in trapping DOC, and their subsequent regulation of global climate, in ancient and modern environments.

Ingredients for early life? Volatile organic compounds in 3.5 Ga old fluid inclusions

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Small organic molecules probably played a central role in the emergence of life on Earth, for instance as building blocks and/or substrates for primeval microorganisms. As yet, however, distinctive candidate molecules have not been found in rocks testifying early life on Earth. Here we report on volatile organic molecules in 3.5 Ga old primary fluid inclusions from the Dresser Formation (Pilbara, Western Australia) [1]. The fluid inclusions are encapsulated within barites which are associated with originally sulfidic stromatolites. Raman spectroscopy and gas chromatography-mass spectrometry demonstrated the presence of CO_2, H_2S and H_2O as well as minor amounts of COS, CS_2, N_2, and CH_4. Furthermore, a wide variety of biologically-relevant oxygen and/or sulfur containing organic molecules were detected. Notably, these include the stable building blocks of methyl-thioacetate (methanethiol and acetic acid) – a putative key-agent in the emergence of life [2]. Our study thus provides the first robust evidence for the existence of primordial organic constituents in early Earth's habitats. Supplied by hydrothermal fluids, these compounds may have fueled early microbial life in the Dresser Formation [1].

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Pyrite formation in microbial mats: Linking the present to the past

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The physicochemical signatures of geological pyrite (FeS_2) – size and shape distribution, trace metal contents, isotopic composition, organic matter association – represent a valuable archive of ancient environments and life. Interpretation of these signatures relies heavily on comparison to modern pyrite, which are mostly forming either in reduced sediments (diagenetic) or in sulfidic water columns such as the Black Sea (syngenetic). However, in the Archean and Proterozoic eons, pyrite formation could also be concentrated in benthic microbial mats that were likely to be widespread [1]. Here, I describe modern pyrite-forming microbial mats from a sulfidic lake system [2]. The pyrite associated with the mats had more variable shapes, narrower size distribution, elevated trace metal contents and more negative iron isotopic compositions than pyrite forming within sediments from the same environment. In addition to pyrite (cubic FeS_2), the mats also contained a substantial portion of the mineral polymorph marcasite (orthorhombic FeS_2), which was absent in the sediments. This work provided strong support as to the unique physicochemical signatures of mat-associated pyrite compared to sedimentary pyrite, with potentially vital implications to reconstruction of ancient environments. A review of the occurrences of pyrite-forming mats in modern systems suggest that that they are either rare or have been overlooked to date. I argue that pyrite formation in modern microbial mats – either as primary deposits or as replacement of precursor elemental sulfur or Fe(III) (oxyhydr)oxides – needs to be better characterized to constrain the extent to which they can affect our understanding of the early Earth.

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^{182}W variations in Paleo-Archean mafic and felsic rocks from the Barberton Greenstone Belt, South Africa

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The short-lived ^{182}Hf-^{182}W decay system is a novel tool to explore geological processes operating during early planetary evolution. Small variations in the isotopic composition of W have been observed in Early Archean mantle-derived rocks and are commonly attributed to either incomplete mixing of 'Late Veneer' material into the mantle [1] or the fractionation of parent and daughter isotopes during silicate and/or metal fractionation within the first 50 Ma years after solar system formation [2]. It has previously been suggested that these anomalous variations in W isotopes in the Archean mantle (expressed as ε^{182}W) were erased due to progressive mixing of these heterogeneous components over time [3]. Yet, more recent studies have reported anomalous ε^{182}W in recent rocks [4,5] suggesting that these heterogeneous components may have been preserved in the mantle over Earth's history. Understanding the W isotopic composition of the mantle over time thus requires a detailed mapping of the temporal as well as spatial occurrence of anomalous ε^{182}W in mantle-derived rocks.

In Eo-Archean terranes, like the Acasta Gneiss complex, positive ε^{182}W anomalies are observed for rock units older than ca. 3.6 Ga, much in line with other terranes of similar age (i.e. Isua Supracrustal Belt [1], Nuvvuagittuq Supracrustal Belt [6], Saglek Block [7]). This pervasive ε^{182}W signature is diminished in younger rocks of the Acasta Gneiss complex (< 3.6 Ga) and slightly later, in the Paleo-Archean Pilbara craton(< 3.2 Ga), due to the progressive homogenization of the mantle [3,8]. Yet, in the Kaapvaal craton, South Africa, negative ε^{182}W anomalies were reported for contemporaneous samples from ca. 3.55 Ga-old komatiites of the Schapenburg greenstone remnant, which were interpreted to be caused by early silicate differentiation of a source enriched in incompatible elements [9]. This finding is contrasted by ε^{182}W values found for slightly younger greenstones, such as those of the 3.45 Ga old Komati formation, that show modern mantle ε^{182}W values close to zero [2]. The presence of a considerable range of ε^{182}W values in mantle-derived rocks over such a relatively short period of time makes the Kaapvaal craton an ideal additional location to study the extent of ε^{182}W variations in the Paleo-Archean mantle.

The 3.55 to 3.53 Ga-old Sandspruit and Theespruit formations of the Kaapvaal craton represent the oldest units of the Barberton Greenstone Belt and mainly consist of strongly deformed mafic-ultramafic metavolcanics rocks, felsic schists and volcanoclastic rocks. Independent geochemical and isotopic data for felsic and mafic rocks of these two formations indicate the presence and mixing of different melt sources [10,11]. These characteristics make the two formations an ideal target to characterize the ε^{182}W of different parental magmas and to elucidate the potential existence and nature of heterogeneous ε^{182}W composition of the Archean mantle underlying the Kaapvaal craton. Accordingly, we report ε^{182}W data for a suite of felsic and mafic rock samples from the Sandspruit and Theespruit formations. Our results indicate a heterogeneous ^{182}W composition, shifting towards negative ε^{182}W anomalies similar to the results for komatiites of the Schapenburg greenstone remnant [8]. We interpret our data in the light of the geochemical as well as tectono-magmatic evolution of the Barberton Greenstone Belt with the aim of investigating potential underlying causes for the perceived W isotope heterogeneity of the Paleo-Archean mantle.

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Emergence of plate tectonic during the Archean: insights from 3D numerical modelling

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In the plate tectonic convection regime, the external lid is subdivided into discrete plates that move independently. Although it is known that the system of plates is mainly dominated by slab-pull forces, it is not yet clear how, when and why plate tectonics became the dominant geodynamic process in our planet. It could have started during the Meso-Archean (3.0-2.9 Ga). However, it is difficult to conceive a subduction driven system at the high mantle potential temperatures (**Tp**) that are thought to have existed around that time, because **Tp** controls the thickness and the strength of the compositional lithosphere making subduction unlikely. In recent years, however, a credible solution to the problem of subduction initiation during the Archean has been advanced, invoking a plume-induced subduction mechanism[1] that seems able to generate plate-tectonic like behaviour to first order. However, it has not yet been demonstrated how these tectonic processes interact with each other, and whether they are able to eventually propagate to larger scale subduction zones.

The Archean Eon was characterized by a high **Tp**[2]**,** which generates weaker plates, and a thick and chemically buoyant lithosphere. In these conditions, slab pull forces are inefficient, and most likely unable to be transmitted within the plate. Therefore, plume-related proto-plate tectonic cells may not have been able to interact with each other or showed a different interaction as a function of mantle potential temperature and composition of the lithosphere. Moreover, due to secular change of **Tp,** the dynamics may change with time. In order to understand the complex interaction between these tectonic seeds it is necessary to undertake large scale 3D numerical simulations, incorporating the most relevant phase transitions and able to handle complex constitutive rheological model.

Here, we investigate the effects of the composition and **Tp** independently to understand the potential implications of the interaction of plume-induced subduction initiation. We employ a finite difference visco-elasto-plastic thermal petrological code using a large-scale domain (10000 x 10000 x 1000 km along x, y and z directions) and incorporating the most relevant petrological phase transitions. We prescribed two oceanic plateaus bounded by subduction zones and we let the negative buoyancy and plume-push forces evolve spontaneously. The paramount question that we aim to answer is whether these configurations allow the generation of stable plate boundaries. The models will also investigate whether the presence of continental terrain helps to generate plate-like features and whether the processes are strong enough to generate new continental terrains or assemble them.

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Syndepositional hydrothermalism selectively preserves records of one of the earliest benthic ecosystems, Moodies Group (3.22 Ga), Barberton Greenstone Belt, South Africa

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The ~3.22 Ga Moodies Group, Barberton Greenstone Belt (BGB), South Africa, provides a unique window into Archaean sedimentary, magmatic and ecological processes. In the central BGB, a regional mafic complex, consisting of a genetically related major mafic sill, a peperitic dyke stockwork, and extensive basaltic lava flows affected thick quartzose sandstones of the Moodies Group. We argue that epithermal hydrothermalism associated with this magmatic event occurred, at least in part, syndepositionally and in places destroyed, in other places preserved the abundant benthic microbial mats in terrestrial- and coastal-facies sandstone of this unit. We differentiate four principal types of hydrothermal alteration: (1) Sericitization resulted from ubiquitous feldspar breakdown; (2) iron-oxide alteration replaced the original matrix by fine-grained iron oxide; (3) silicification replaced matrix and most non-silica grains by microcrystalline silica and locally preserved kerogenous microbial mats; and (4) hydraulic fracturing at shallow depth brecciated consolidated Moodies Group sandstone and created closely spaced, randomly oriented fractures and quartz-filled veins. Because stockwork intrusion locally interacted with unconsolidated water-saturated sediment and because the dykes connect the sill with the mafic lava but also follow zones of structural weakness, we suggest that hydrothermalism associated with this magmatic event occurred syndepositionally but was also – within the resolution of radiometric age data – contemporaneous with tight regional folding. We conclude that microbial organisms in Paleoarchaean coastal (tidal, estuarine) environments may have been formerly widespread, possibly even abundant, but are nearly nowhere preserved because they were easily degradable. Preservation of Early Archaean microbial mats in a thermal aureole in the central BGB was controlled by the "just right" degree of heating and very early hydrothermal silicification.

Remnants of anaerobic phototrophic benthic mats in the 3.46 Ga Marble Bar Chert Unit (Pilbara, Western Australia)

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The 3.46 Ga Marble Bar Chert (MBC) of the East Pilbara Terrane is one of the most unique bedded chert facies in this region and shows features indicative for a large complex silicate-chert mound, c. 200 m thick and 30 km long, formed in open water. The MBC is deposited on the 3.465 Ga basaltic Duffer-Formation, and overlain by pillow basalts of the 3.458 Ga mafic-ultramafic Apex Formation. Parts of the drill core ABDP 1 [1] were re-investigated to screen black layers for geochemical biosignatures and microbial remnants. The lower part of the MBC section is characterized by cm thick kerogenous black layers in a white to gray chert matrix (zone 1–2). The upper part of the section is characterized by BIF-type hematite layers, and red jasper-rich facies (zone 3–5). The kerogenous black laminated layers were analyzed in detail by Raman spectroscopy, µ-XRF, XRD, FEM-EDX, and organic geochemistry ($\delta^{13}C$ via IRMS). These cm thick organic layers exhibit a clear fine lamination of less than 1 mm and resemble a typical microbial mat structure. For instance, the organic material consists of c. 5–10 µm sized black organic grains that form ball-shaped aggregates, resulting in a clear thrombolytic fabric which is typical for some microbial facies. Based on 2D and 3D Raman images, two distinct areas are recognized, a lower one rich in reduced Fe minerals like pyrite and siderite, and an upper one with oxidized Fe minerals like magnetite and hematite. 2D Raman images of the lower part of the mat structure exhibit small anhedral pyrite crystals interwoven with organic material, and small siderite crystals. In the upper part of the mat unit, the 3D images reveal abundant small magnetite and hematite crystals interwoven in the organic matrix. It seems plausible that oxidized Fe-species were formed diagenetically through alteration of biogenic ferrihydrite, which was formed via anaerobic photoferrotrophic microbes [2–4]. Notably, $\delta^{13}C_{org}$ values of kerogenous material range proximately between ca. −12 and −25‰. This is significantly heavier than normally observed in early Archaean organic matter [5], and potentially indicates C-fixation via anaerobic photosynthesis. In conclusion, the observed organic layers at the base of the Marble Bar drill core section are interpreted as complex benthic microbial mats formed by photoferrotrophic and sulfate reducing microorganisms.

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Stable W and Mo isotopic data support increasing redox potentials of the Archean ocean through time

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The stable tungsten (W) isotope system has lately been the target of a number of studies investigating its potential as a new marine redox proxy. Dissolved W (as WO_4^{2-}) adsorbs onto Fe- and Mn-oxides with associated equilibrium stable isotopic fractionations $\varepsilon^{186/184}$W of 0.51 and 0.59 ‰, respectively [1], resulting in isotopically heavy modern seawater ($\delta^{186/184}$W = +0.55 ‰ [2]) compared to the detrital input source from the continents (-0.01 to +0.10 ‰). Interestingly, W unlike Mo is not quantitatively scavenged into euxinic sediments through thiolation reactions, but is strongly authigenically enriched in shales deposited under hypoxic/anoxic conditions [3]. This observation together with the lower redox potential of WO_4^{2-} compared to that of MoO_4^{2-} may allow the stable W isotopic composition of Archean shales to be a very sensitive tool to investigate changes in the redox state of the ferruginous Archean ocean.

We tested this hypothesis by measuring the stable W isotopic composition of well-characterized 3.47, to 2.50 Ga old marine black shale suites deposited under ferruginous conditions (Archean Biosphere Drilling Project, Pilbara Craton, Australia). Determination of the $\delta^{186/184}$W values of Archean-Paleoproterozoic igneous rocks to establish the detrital isotopic signal of contemporary shaly sediments revealed the same $\delta^{186/184}$W range than for modern igneous rocks. All shale suites show mixing trends in $\delta^{186/184}$W values from this detrital background towards an isotopically heavier endmember of up to +0.246 ‰. Our observation indicates that the hexavalent W in form of WO_4^{2-} marine W redox cycling must have existed in the Archean ocean as early as 3.47 Ga. However, all these samples with the exception of the youngest 2.5 Ga shales suite have crustal-like $\delta^{98/95}$Mo values, whereas fractionated $\delta^{98/95}$Mo signatures have been reported for up to 2.93 Ga old shallow marine carbonates [4]. Combining all these information, we devise a multi-step redox evolution model for the Archean ocean, showing continuously increasing redox potentials Eh from shallow to deep ocean water masses.

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A tsunami deposit in the ca. 3.48 Ga Dresser Formation (Pilbara Craton, Western Australia) – Implications for early Archean sedimentary processes

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Intense meteorite bombardment likely influenced Earth's earliest habitats. Such impact events potentially triggered tsunamis, which might leave distinct sedimentary traces, as for instance high-energy deposits in low-energy depositional environments. However, the early Archean record of such deposits is sparse. Here we report a sedimentary succession in the ca. 3.48 Ga Dresser Formation (Pilbara Craton, Western Australia) that contains evidence for temporary high-energy conditions and possibly reflects an impact-related tsunami. Particularly noteworthy are two distinct debrite-turbidite couplets that are characterized by Bouma-type sequences and bi-directional current indicators (e.g. reversely imbricated clasts). Notably, some of these imbricated clasts are up to 10 cm across, indicating erosion and transport under high-energy conditions. It is tempting to speculate that hydrodynamic processes were influenced by the presence of dense, highly silica-rich seawater. Regardless of these potentially non-actualistic conditions, the observed features are best explained by the passage and rebound of a tsunami wave. Taken together, our results provide a comprehensive set of sedimentological criteria that may help to track earthquakes and/or impact events through geological time and to evaluate their meaning for the early evolution of life on Earth.

Biogenic Carbon in Magmatic Minerals and Implications for the Preservation and Obliteration of Hadean Isotopic Biosignatures

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The first few 100 million years of the solar system are a critical period during which life possibly already emerged on Earth. Graphite inclusions in detrital zircon have been interpreted to contain C isotopic signatures for biologic activity with $\delta^{13}C_{PDB}$ = -24 ± 5 ‰ already by 4.1 Ga [1], but how graphite may have entered magmatic zircons and preserved isotopic signatures since then remains incompletely understood. Reliable interpretation of potential biosignatures in crystalline rocks requires understanding of how the near-surface C-cycle interacts with magmatic environments where graphite is entrapped in igneous zircon. To amend this lack of knowledge, zircons from graphite-bearing granite of Phanerozoic age are studied.

In a first step, sample preparation procedures were established to avoid C contamination and secondary reference materials for C isotope analysis was characterized because primary references like USGS24 graphite ($\delta^{13}C_{VPDB}$ = -16.049 ± of 0.035‰ [2]) are only homogeneous at the scale of bulk analysis, whereas localized SIMS analysis (beam spot diameter ~1–2 µm) indicates heterogeneity of ~0.9‰. Two graphite samples from Sri Lanka (Heidelberg collection) yield bulk $\delta^{13}C_{VPDB}$ of -6.615 ± 0.109 and -5.730 ± 0.026‰ and SIMS uncertainties of 0.35 and 0.22‰, respectively, indicating that these materials are more homogeneous than USGS24 at the µm-scale.

Graphite-bearing granite of the Rumburk pluton from the border region of Germany, Poland, and Czech Republik was sampled along with metasedimentary country-rock (six granitic and five schist samples). For the schists, bulk $\delta^{13}C_{VPDB}$ analysis indicate values between -21.82 and -24.26‰; considered as benchmark for the potential source composition of C in the granite. Zircon U/Pb geochronology and trace element analysis of the Rumburk granite confirms a Cambro-Ordovician age. Zircon U concentrations vary between 70 and 3600 ppm (Th/U ratio between 0.04 to 0.9, mainly between 0.2 to 0.5). The lack of a positive Ce anomaly of many zircon grains (mostly at the rim analysis of the zircon grains) indicates crystallization from a highly reduced melt. The Ti thermometer for the analysed zircon grains indicates a crystallization temperature of ~600-900°C, mostly around ~700°C. Opaque inclusions in zircon identified by micro-Raman analysis are predominantly ilmenite; three graphite inclusions as well as carbonate were identified in the ongoing search. Carbon isotopic analysis by SIMS of graphite in zircon and in-situ in schists is pending to assess potential fractionation during high-grade metamorphism and anatexis.

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Towards making habitable Earths: the importance of pre-natal physical and chemical conditions

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One of the most intriguing scientific questions is to understand conditions necessary to making a ha bitable planet, like our Earth. To answer these questions, we modeled the evolution, distribution, and abundances of the key ingredients for life – water, carbon-, nitrogen-, and sulfur-bearing compounds in the solar nebula and other similar objects. We focused on the overall chemical composition and elemental ratios such as C/O, N/O, C/H, N/H, D/H etc., which may provide important links to the chemical and isotopic composition of Earth and earth-like planets, gas giants as well as primitive bodies such as meteorites and comets. In my talk, I will present a detailed model of the solar nebula & protoplanetary disks that includes gas and dust structures, high-energy radiation, and gas-grain time-dependent chemistry. Using this model, we calculated radial and vertical distributions of the elemental ratios in the gas and ice phases as well as gas/ice partitioning of volatiles for variety of physical conditions (disk gas mass, density, size, etc.). I will show the spatial distributions of the major C-, O-and N-bearing gas-phase molecules and ices, and that the local C/O and N/O ratios can significantly deviate from the initial elemental ratios. Furthermore, the destruction of carbonaceous grains and Insoluble Organic Matter-like compounds in the very inner nebular region could also affect the local C/O ratios and reduce the amount of refractory carbon in the zone of terrestrial planet formation.

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Triple oxygen isotopes systematics and clumped isotopes of carbonates – a combined approach using high-resolution isotope ratio mass spectrometry to understand early Earth's sediment record.

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$\delta^{18}O$ signatures in early Earth's chemical sediment record show a secular shift towards lower values compared to Phanerozoic and modern carbonates that may result from i) a 'hot' Archaean ocean, ii) an ancient ocean that was significantly lower in $\delta^{18}O$, or iii) post-depositional re-equilibration of the old sediment record. Combined analysis of $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ($\Delta'^{17}O = \ln(\delta^{17}O+1) - 0.528 \cdot \ln(\delta^{18}O+1)$) provides a valuable tool to resolve these scenarios. Recent $\Delta'^{17}O$ isotope analysis of cherts has shown that 'hot' Archaean ocean water may not explain the observed isotopic shift [1].

We analyzed triple oxygen isotopes of carbonates by means of fragment ion analysis ($^{17}O^+/^{16}O^+$ and $^{18}O^+/^{16}O^+$) of liberated CO_2 with a *Thermo Scientific Ultra* high-resolution gas source isotope ratio mass spectrometer (HR-IRMS). Carbonate $\Delta'^{17}O$ data are in agreement with findings from chert analysis but do yet not resolve whether a low $\delta^{18}O$ ocean (scenario ii) or diagenesis (scenario iii) ultimately determine the isotopic composition.

Here, we present the current state of $\Delta'^{17}O$ fragment ion measurements and discuss its potential and limitations. We also present first data of doubly-substituted isotopologue distribution ('clumped' isotopes) analyzed by HR-IRMS, which provide a tool to reconstruct carbonate equilibration temperatures independent of the isotopic composition of ambient waters [3]. We discuss how the combined analysis of Δ_{47} and Δ_{48} along with $\Delta'^{17}O$ of Archaean carbonates reciprocally improves evaluation and interpretation of both approaches.

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How did Cyanobacteria survive increased atmospheric O_2 levels during the Great Oxygenation Event? The role of Superoxide Dismutases (SOD).

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Cyanobacteria, as the only extant prokaryotes known to conduct oxygenic photosynthesis, are attributed with the oxygenation of the early Earth's atmosphere during the great oxygenation Event (GOE). While routinely exposed to daily cycling of localized O_2 enrichment in their immediate environment, the effect of increasing levels of atmospheric O_2 on the physiology of Cyanobacteria is unknown. Oxidative damage is caused by reactive oxygen species (ROS) generated as intermediates of O_2 reduction or energization within the cell. In this project we investigate the expression of one of the primary enzymes involved in eliminating the superoxide ion, $O^{2\bullet-}$, from Cyanobacteria, namely the Superoxide Dismutase (SOD) enzymes identified in the basal marine species, *Pseudanabaena* sp. PCC7367.
Growth curves based on cellular Chlorophyll a content were conducted to compare the growth rates of *Pseudanabaena* sp. PCC7367 under an Archean anoxic atmosphere, our Present Atmospheric Level (PAL) of CO_2 and O_2, and a PAL atmosphere supplemented with CO_2 levels matching those of the Archean simulation (0.2%). Expression of three SOD genes identified in *Pseudanabaena* sp. PCC7367, namely the manganese-based SOD isoform, MnSOD, the iron-based SOD isoform, FeSOD and the copper and zinc containing isoform, CuZnSOD, was monitored over a full day night cycle using the quantitative gene amplification method, reverse transcription polymerase chain reaction (RT-qPCR).
The growth rate for *Pseudanabaena* sp. PCC7367 was faster for cultures grown under the anoxic atmosphere compared to the control PAL cultures and those grown at elevated CO_2 and PAL levels of O_2. These data suggest that modern levels of atmospheric O_2 impairs the growth of Cyanobacteria compared to those grown under a simulated anoxic Archean atmosphere. Our results support the data presented in Herrmann et al. (2021) that indicates higher O_2 production rates in *Pseudanabaena* sp. PCC7367 grown in an Archean simulated anoxic atmosphere, than under PAL conditions.
Expression of the cytoplasmic FeSOD appears to be constitutive over the day:night cycle, with the membrane bound CuZnSOD appearing to be upregulated at night. MnSOD, which can be located in the cytoplasm or membrane-bound, increased its expression with increasing levels of oxygen in its environment.
Our study thus far suggests that early Cyanobacteria, growing in an anoxic atmosphere, were able to grow faster than under present day levels of O_2. We propose that the expression levels of all SODs, particularly those of the MnSOD, will be increased in cultures of *Pseudanabaena* sp. PCC7367 grown under modern day levels of O_2. Furthermore, whether this increased expression relates to increased enzyme synthesis will be determined using activity assays in the future. By the end of this study, we will have a better understanding of how Cyanobacteria dealt with oxygen free radicals during the Archean, and also how Cyanobacterial oxygenic photosynthesis may be affected under elevated atmospheric CO_2 levels resulting from climate change.

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NOTE: Ms. Sadia Tamanna is currently completing her MSc in the GeoMicrobiology laboratory at the TU Kaiserslautern.

Recycled roots of Hadean protocrust – A possible OIB endmember?

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In recent models, deficits of ^{182}W in modern OIBs are explained by a primordial reservoir in the lower mantle that mixes with classical mantle endmember components DMM, EM1, EM2, and HIMU [1]. Yet the exact origin of the low ^{182}W endmember in modern OIBs is not known. Popular models argue that negative ^{182}W isotope anomalies originate from core-mantle interaction either by chemical exchange or by isotopic equilibration [2,3]. Understanding the origin of this mantle reservoir and its evolution in the geologic past is of great importance to resolve the ^{182}W dichotomy between modern OIBs and most Archean mafic rocks that largely display positive ^{182}W anomalies. Notably, Archean rocks from the Kaapvaal Craton, southern Africa, are unique in this regard, as they were shown to be the only known Archean rocks displaying negative ^{182}W isotope anomalies. To better understand the origin of these ancient signatures we performed high-precision ^{182}W isotope measurements on a wide selection of rocks from the Kaapvaal Craton that were previously analyzed for ^{142}Nd [4] and combine our results with constraints from long-lived ^{176}Hf-^{143}Nd-^{138}Ce and trace element systematics to better characterize their parental mantle sources. All these parameters were then combined to develop a geodynamic model that reconciles all observational constraints. We can show that lower crustal Hadean-Early Archean restites from prolonged TTG formation were recycled into the upper mantle and significantly contributed to mafic magmatism in the Kaapvaal Craton. If preserved in the modern mantle, such recycled components may even account for ^{182}W deficits in modern OIBs. In this regard, our model constitutes a viable alternative explaining the origin of primordial components in the source region of modern OIBs, thus bridging between ^{182}W isotope systematics in Archean mantle derived rocks and their modern-day counterparts.

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Searching for an inorganic signature of life in modern microbial mats

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Coastal environments present harsh conditions for multicellular organisms due to the large gradients in salinity and redox potential combined with low nutrient availability, possibly somewhat analogous to conditions on early Earth. Modern cyanobacterial mats forming in such environments may, therefore, represent a useful opportunity to apply inorganic geochemical redox proxies, such as uranium isotopes (^{238}U/^{235}U), to assess if there is an inorganic signature for bacterial life, e.g., biotic U reduction. In this study, we sampled microbial mats forming on the supratidal sands and adjacent dunes of the Dutch barrier island Schiermonnikoog in the North Sea. Biocrusts were sampled from four sites with various coloured horizons present (brown/green: cyanobacteria with carbonation, pink: purple sulphur bacteria and black: iron sulphide formation). A shallow soil profile was also sampled at one site between the biocrust and the groundwater table. Supratidal sands without visible biocrust development were also sampled to assess the composition of the substrate. In addition to U isotopic analyses, we measured total carbon (TC) and trace element concentrations.

The δ^{238}U of biocrust and soil samples ranged from -0.14 to -0.29 ‰, whereas the sand samples ranged from -0.24 to -0.28 ‰. The maximum δ^{238}U was found in the soil profile, accompanied by higher S and Mo contents, which may be attributed to abiotic U reduction or microbial processes under sulfidic conditions. The biocrust δ^{238}U ranged from -0.28 to -0.21 ‰, largely reflecting the substrate. However, high TC contents in the biocrusts of up to 2.7 % relative to the substrate (~0.2%) confirm the active accumulation of organic matter and/or (microbial) carbonate precipitation. As there is a high proportion of U in the silicate fraction, which is non-redox active, any U isotope fractionation in the bulk samples might have been obscured. Thus, we will conduct sequential extraction to isolate the different non-detrital phases and determine whether there is any U isotope fractionation associated with U reduction.

The effect of fractional crystallization on the volatile release from intrusive bodies on early Earth

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The atmosphere on early Earth is crucial for the emergence and evolution of life. After intense destruction of the primary atmosphere and the crystallization of the magma ocean, magmatic outgassing is the main volatile source. It influences the formation and composition of the secondary atmosphere strongly and thus the habitability of the Earth. The outgassing process includes the well-studied extrusive as well as the often neglected intrusive volatile release. However, it is assumed that the intrusive magma production rates are significantly higher compared to extrusive rates. This renders the investigation and quantification of possible volatile release mechanisms from intrusive magma systems essential.

The process of fractional crystallization within a magma body has an influence on the solubility and thus on the associated volatile release. Due to cooling of an intrusion, nominally anhydrous minerals precipitate from the melt. These minerals mainly incorporate elements that are compatible with their crystal lattice. Since volatiles such as H_2O and CO_2 behave like incompatible elements, they accumulate in the remaining melt. At a certain point, the melt is saturated and the exsolution of a volatile phase initiates. The solubility of the volatiles is determined by several parameters like the lithostatic and the partial pressure, the temperature and the melt composition. In this study, we investigate the effect of these parameters as well as the impact of the volatile accumulation due to fractional crystallization on the solubility and the related volatile exsolution. We focus on the release of H_2O and CO_2 from basaltic magma bodies within the lithosphere. To determine the fate of the accumulating volatiles, we compare the density of the developing melt with the density of the host rock. If the host rock has a higher density, the liquid phase (melt and volatiles) will ascent either directly to the surface or to shallower levels of the crust. Furthermore, we take into account the possible effect of the precipitation of hydrous minerals (e.g., amphibole) during the crystallization process.

Volatile element abundances in Apollo samples determined by isotope dilution ICP-MS

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Most likely due to its impact origin, Earth’s Moon is more strongly depleted in volatile elements like Cu, Zn and Cd than Earth. The volatile element contents of lunar samples, such as soils, (impact) breccias, basalts and highland lithologies are affected by many additional processes such as degassing, vapor deposition, micrometeorite bombardment, mixing and mineral melt partitioning. In order to provide a better understanding of these processes in different lunar settings, we will analyze twelve soils, five basalts, five highland rocks, four breccias and one pyroclastic deposit for their Cu, Zn, Ga, Ag, Cd, In, Sn, and Tl contents by isotope dilution ICP-MS [1]. In addition, major and trace element analyses will be conducted using conventional ICP-MS. So far, six Apollo samples and two leachates thereof were investigated along with their Cd isotope composition [2].

On average, an orange glass soil sample displays the highest volatile element contents (>0.1 x CI for all elements determined by isotope dilution). These elements were near quantitatively removed from the sample powder, when treated with cold 2 M HCl. All other elements are only removed to about 30%. This observation and the light Cd isotope composition of the orange glass soil [2] is in line with volatile element deposition as vapor coatings around lunar glass beads that formed during lunar fire fountaining [e.g., 3].

One highland and one mare soil sample display much higher volatile element abundances than their igneous counterparts, especially for Ag, Zn, Cd, In and Tl. Furthermore, both soil samples display higher In abundances than CI chondrites. This observation renders contamination by meteorites as the primary cause of volatile element enrichment in lunar soils [e.g., 4] unlikely and rather suggests a lunar igneous source for the volatile element enrichment in the soils [e.g., 5].

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Paleoarchean carbonates – important archives for early Earth's environments

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Early Archean carbonates from the Pilbara Craton (Western Australia), Barberton Greenstone Belt (South Africa), and Isua (Greenland) occur in a variety of facies. In the Pilbara, for instance, these facies include ca. 3.5–3.4 Ga old pillow-basalt interspaces (North Star Basalt, Mt. Ada Basalt, Apex Basalt, Euro Basalt), ca. 3.5 Ga old hydrothermally formed bedded chert-carbonates (Dresser Formation), and ca. 3.4 Ga old stromatolites (Strelley Pool Formation). The carbonates exhibit variable mineralogies, ranging from calcite, through dolomite to Fe/Mn-rich dolomite (ankerite/kutnahorite). At Isua, carbonates of disputed origin occur for example in 3.7 Ga old rocks from the 'stromatolite site' [1, 2, 3]. The Pilbara carbonates were formed *via* the following pathways:

1. Abiotic precipitation: Carbonates in pillow-basalt interspaces precipitated abiotically from highly alkaline brine solutions as indicated by δ^{13}C-values (ca. 0±1‰). All these carbonates have characteristics indicating mixing between seawater and igneous rocks. There is a weak LREE depletion, La/La* is weakly positive or absent, Y/Ho is superchondritic but lower than modern seawater. The formation of these precipitates was linked to intense pumping of seawater through the oceanic crust – likely a significant sink for CO_2 in Archean seawater.
2. Organomineralization *sensu* [4]: This carbonate formation pathway is evidenced by an intimate association between mineral precipitates and organic matter. Two groups can be distinguished:
    a. Fine-grained sedimentary carbonates in the Dresser and Strelley Pool Formations. These include dolomites and calcites which precipitated from seawater with elevated alkalinity, as reflected in δ^{13}C-values of ca. 0 –1.5‰.
    b. Carbonate crystals in bedded cherts of the Dresser Formation. These include Mn/Fe-rich dolomites (kutnahorite partly) and other dolomitic carbonate minerals that precipitated in low temperature hydrothermal pond environments. The hydrothermal influence is e.g. reflected in relatively low δ^{13}C-values of the carbonates (ca. –6‰), indicating a magmatic/mantle origin of the CO_2 and a strong positive Eu/Eu* anomaly characteristic for hydrothermal influence. The precipitates commonly encapsulate putative microbial remnants and so potentially form excellent mineral matrices for biosignatures for testing the presence of life in ancient hydrothermal settings. There is no evidence for marine influence.
3. Microbially mediated mineralization: Stromatolites in the Strelley Pool Formation almost entirely consist of dolomites [5]. Carbonate formation was probably coupled to anoxygenic photosynthesis. $\delta^{13}C_{carb}$-signatures of ca. +4‰ indicate probably a strong C-fixation via photosynthesis and REE+Y characteristics is indicative for seawater. It appears likely that the process was already linked to microbial exopolymeric substances (EPS).

The 3.7 Ga Isua carbonate of the 'stromatolite' site has a seawater REE+Y pattern (LREE-depletion, positive La/La*-anomaly, superchondritic Y/Ho ratio), in line with earlier observations [3, 5].]. We additionally analyzed a metasomatic talc-rich carbonate from this locality for comparison. Notably, the talc-rich carbonate is clearly distinct, showing a chondritic Y/Ho-ratio, no La/La*-anomaly, but also a LREE-depletion. These characteristics are in line with a seawater source that strongly interacted with (ultra)mafic crust.

This brief review on Paleoarchean carbonates demonstrates their enormous diversity, which is still highly underestimated. A better understanding of their distribution and formation pathways will help to track microbial activity on the early Earth and to reconstruct the geobiology of Paleoarchean environments. It has also wide implications for biogeochemical cycles on the early Earth, as carbonates may formed efficient CO_2 sinks.

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