

Abstracts

of the Second General Meeting

"Early Earth evolution"

March 29-31, 2017

Jena



PROGRAMME

General Meeting 2017 SPP 1833 "Building a Habitable Earth" Institute for Inorganic and Analytical Chemistry Humboldtstr. 8, Jena

Wednesday, March 29th: Early Solar System

14.00-14.15	Carsten Münker, Köln & Christoph Heubeck, Jena: Introductory remarks
14.15-14.30	Christian Vollmer, Münster: The carbon and nitrogen functional chemistry of organic matter in extraterrestrial samples
14.30-14.45	Jan Leitner, Mainz: Characterization of Nitrogen-bearing phases in Enstatite Chondrites
14.45-15.00	Ninja Braukmüller, Köln: Elemental analyses of bulk carbonaceous chondrites with SF-ICP-MS
15.00-15.15	Christian Lenz, Heidelberg: Constraining the Parameter Space for the Solar Nebula
15.15-15.30	Natascha Manger, Heidelberg: Vortex Formation through hydrodynamic instabilities
15.30-15.45	Manfred Vogt, Heidelberg: Volatile acquisition during terrestrial accretion: Solar wind (SW)-implanted Ne in cosmic dust
15.45-16.15	Coffee Break
16.15-16.30	Wladimir Neumann, Münster: Ceres – a water-rich precursor to fill Earth's oceans
16.30-16.45	Mario Fischer-Gödde, Münster: Ruthenium isotopic evidence for an inner solar system origin of the late veneer
16.45-17.00	David Rubie, Bayreuth: A scaling law for melt volume produced by giant impacts
17.00-17.15	Sylvain Petitgirard, Bayreuth: Density and structure of amorphous silicate at high pressure conditions
17.15-17.30	Katherine Armstrong, Bayreuth: Iron speciation in silicate melts as a function of pressure: implications for magma ocean and early atmosphere evolution
17.30-17.45	Maxim Bykov, Bayreuth: Novel iron nitrides synthesized at the conditions of the deep Earth's interiors
17.45-18.00	Ulrich Hansen, Münster: Evolution of a bumpy core-mantle boundary from a chemically stratified mantle
18.30	optional: Joint Dinner in a local pub

Thursday, March 30th: Onset of Plate Tectonics and Continental Crust Formation

9.00-9.30	Nicholas Arndt, Grenobles (Keynote): The Onset of Plate Tectonics and Significance (if any) of the Archean-Proterozoic Boundary
9.30-9.45	Richard W. White, Mainz: Phase equilibrium constraints on the formation and evolution of Earth's earliest continental crust
9.45-10.00	Andrea Piccolo, Mainz: Geodynamical implication of delamination on felsic crust generation during the Archean
10.00-10.30	Coffee Break
10.30-10.45	Matthias Schmitz, Jena: Horizontal vs Vertical Tectonics in the Barberton Greenstone Belt
10.45-11.00	Sampriti Basak, Bochum: Multistage evolution of Coorg granulites, S. India – constraints on timescales of evolution
11.00-11.15	Annika Dziggel, Aachen: Exhumation of deep crustal granulites during Neoarchean terrane accretion in the Nuuk region, SW Greenland
11.15-11.30	Jochen Kolb, Karlsruhe: The Godthåbsfjord gold province in the North Atlantic craton of southern West Greenland
11.30-11.45	Christian Marien, Köln: Fiji: Probe of ancient continental growth?
11.45-13.15	Lunch Break

Note that only the first author/speaker of each talk is given, all co-authors are cited in the abstracts



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Thursday, March 30th: Isotopes

13.15-14.15	Meeting of the Scientific Committee & Proposals for the second phase of the SPP 1833
14.15-14.30	Stefan Peters, Göttingen: Triple oxygen isotope compositions of Archean ultramafic rocks
14.30-14.45	Jonas Tusch, Köln: High-precision W isotope measurements on Archean rocks from the Isua area, South-West Greenland
14.45-15.00	Sebastian Viehmann, Wien: The potential of coupled Hf-Nd isotopes to unravel geodynamical processes on Early Earth
15.00-15.15	Jens Hopp, Heidelberg: Search for palaeoatmospheric noble gas isotopes
15.15-15.30	Kathrin Schneider, Berlin: Implications of 146Sm-142Nd systematics on Paleoarchean volcanic and granitoid rocks from the eastern Kaapvaal Craton
15.30-16.00	Coffee Break
16.00-16.15	Elis Hoffmann, Berlin: A geodynamic model for the lower Onverwacht Group, Barberton Greenstone Belt (South Africa)
16.15-16.30	Alfred Kröner, Mainz & Elis Hoffmann, Berlin: Were early Archaean greenstone belt remnants in the eastern Kaapvaal craton, southern Africa, part of a large continental plateau basalt province?
16.30-16.45	Sukanya Sengupta, Göttingen: Geochemical modelling of triple oxygen isotope composition of seawater using high precision Δ '17O analyses of terrestrial materials
16.45-17.45	Poster Session
18:00	Reception at the special exhibition "Die Erde im Archaikum – Leben erobert einen Planeten" (optional)

Friday, March 31th: Early Life

9.00-9.30	Mark van Zuilen, Paris (Keynote): Biogenic and abiogenic microstructures in the early rock record
9.30-9.45	Dieter Braun, München: Early life driven by thermal forces in pores of rock?
9.45-10.00	Helge Mißbach, Göttingen: The fate of biogenic vs. abiogenic organic matter during thermal maturation
10.00-10.15	Jan-Peter Duda, Göttingen: Where geo- meets astrobiology: Tackling the origin of organic matter on early Earth
10.15-10.30	Christian Hallmann, Bremen: Indigenous and non-indigenous Precambrian hydrocarbons: what Information can we extract about Earth's earliest biota?
10.30-11.00	Coffee Break
11.00-11.15	Christoph Heubeck, Jena: A Paleoarchean coastal oxygen oasis, Moodies Group, Barberton Greenstone Belt
11.15-11.30	Sami Nabhan, Jena: Biogenic overgrowth on detrital pyrite in ~3.2 Ga old Archean paleosols (Moodies Group, BGB, South Africa).
11.30-11.45	Stefanie Gebauer, Berlin: Effect of geologically-constrained environmental variables on the atmosphere and biosphere of early Earth
11.45-12.00	Michelle Gehringer, Kaiserslautern: Oxidative photosynthesis before the Great Oxygenation Event
12.00-12.15	Gerhard Franz, Berlin: Algal bloom in a Paleoproterozoic pegmatite from Volyn, Ukraine - an example of geo-bio-interaction in the early Earth history
12.15-12.30	Inga Köhler, Jena: First geochronologically-resolved Meso-Archean O_2 production
12.30-12.45	Conclusion

Note that only the first author/speaker of each talk is given, all co-authors are cited in the abstracts



Posters

General Meeting 2017 SPP 1833 "Building a Habitable Earth" Institute for Inorganic and Analytical Chemistry Humboldtstr. 8, Jena

Nina **Albrecht**, Göttingen: Analyzing Δ^{17} O of sedimentary carbonates by means of high resolution mass spectrometry in order to establish a new single phase thermometer

Annika **Brüske**, Hannover: Constraints on metal mobilization in early Proterozoic marine sediments from Uranium isotopes

Paul **Fugmann**, Jena: Petrology, geochemistry and age of the syn-Moodies Lomati River Sill in the Barberton Greenstone Belt

Arne Leider, Bremen: Diagnosticity of steroidal breakdown products in pyrolysates

Isabelle Leisgang, Mainz:

LA-ICP-MS zircon ages for clastic sediments of the Moodies Group, Barberton Greenstone Belt, South Africa and Swaziland

Christian Maas, Münster:

Effect of planetary rotation on the differentiation of a terrestrial magma ocean

Raul Martinez, Freiburg:

Surface reactivity of the anaerobic phototrophic Fe(II)-oxidizing bacterium *Rhodovulum iodosum*: implications for trace metal budgets in ancient oceans and banded iron formations

Franziska Scheffler, Potsdam:

Evaporite pseudomorphs in the Paleoproterozoic Koegas Fm., South Africa

Ronny Schönberg & Michael Babechuk, Tübingen:

Fe & Cr isotopes of the ca. 2.45 Ga Cooper Lake paleosol: anoxic weathering in the wake of the GOE

Toni Schulz, Wien:

New insights into the Paleoarchean meteorite bombardment of the Earth - Geochemistry and Re-Os isotope signatures of the BARB5 ICDP drill core from the Barberton Greenstone Belt, South Africa

Falko **Schulz** & Nicola **Tosi**, Berlin: Early mantle dynamics with non-linear rheology

Jie **Yao**, Bayreuth: Liquid and glass structure of Mg2SiO4 and MgSiO3 at high pressure

Map of the conference venue



All abstracts are given in alphabetical order of the first author

Analyzing Δ^{17} O of sedimentary carbonates by means of high resolution mass spectrometry in order to establish a new single phase thermometer

Albrecht*, N., Pack, A.

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Archean sedimentary carbonates have ~15‰ lower δ^{18} O than their Phanerozoic counterparts [1]. This is controversially discussed to be either due to hot ancient oceans [2], low δ^{18} O of Archean ocean water [3], or diagenetic interaction with low δ^{18} O fluids [4]. We target to shed light on this long-standing debate by applying a new single phase thermometer, making use of high precision data on δ^{17} O and δ^{18} O obtained with a high resolution mass spectrometer ThermoScientific[®] MAT253 Ultra. We present initial progress in our analytical protocol on measuring oxygen fragments of CO₂ with a precision <10 ppm. This includes the exploration of the technical limits of the mass spectrometer, a suitable procedure to prepare the sample gas, and the production of an appropriate CO₂ standard for Δ^{17} O.

[1] Jaffrés, J.B.D. et al. (2007) ESR 83, 81–122.

- [2] Robert, F., Chaussidon, M. (2006) Nature 443, 969–972.
- [3] Shields, G.A., Kasting, J.F. (2007) Nature 447, E1–E1.
- [4] Blake, R.E. et. al (2010) Nature 464, 1029–1032.

Iron speciation in silicate melts as a function of pressure: implications for magma ocean and early atmosphere evolution

Armstrong*, K.; Frost, D.J.; Rubie, D.; McCammon, C.M.; Boffa-Ballaran, T. *Bayerisches Geoinstitut, Universität Bayreuth, Universitätstrasse 30, Bayreuth, 95447 Katherine.armstrong@uni-bayreuth.de

During differentiation, mantle silicates must have been in equilibrium with core-forming metal iron, as indicated by the depletion of siderophile elements from the mantle. Studies of ancient rocks suggest that by at least 3.9 Ga, the upper mantle was 4-5 log units more oxidized than metal saturation implies [1]. The oxidation process is unclear, but has implications for the timing of volatile delivery to the early Earth, as well as evolution of the early atmosphere. One possibility is suggested by the tendency of high-pressure silicate minerals to favour Fe3+ over Fe2+ in their structures, even at metal saturation. In the lower mantle, this tendency in the mineral bridgmanite has been proposed to drive the disproportionation reaction of FeO to form Fe2O3 and iron metal [2]. We have performed experiments at the Ru-RuO2 fO2 buffer and at metal saturation which show that silicate melts may mirror this behaviour and Fe3+ may be stabilized with pressure for a constant fO2; by 21 GPa, the previously observed trend of Fe3+ decreasing with pressure [3] reverses and ferric iron content had increased (figure). FeO disproportionation may have occurred at the base of an early magma ocean, establishing a redox gradient similar to what is presumed for the mantle today.



[1] Delano (2001) Orig. Life. Evol. Biosph. 31, 311–341.

^[2] Frost (2004) Nature 428, 409-412.

^[3] O'Neill et. Al. (2006) Am. Min. 91, 404-412.

Fe & Cr isotopes of the ca. 2.45 Ga Cooper Lake paleosol: anoxic weathering in the wake of the GOE

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The element and stable isotopic geochemistry of redox sensitive elements (e.g., Cr) within paleosols and marine sedimentary rocks have contributed to reconstructing the timing and nature of the rise of atmospheric oxygen before and during the "Great Oxidation Event" (GOE, starting ca. 2.45 Ga). The current model adopted to explain fractionation of Cr stable isotopes in modern and ancient surface environments requires oxidative continental weathering by which Cr(III) is oxidised to Cr(VI), catalysed by Mn(III)/(IV)-oxides (often biological driven). It has been hypothesized that this process induces reservoir isotopic fractionation when isotopically heavy and soluble aqueous Cr(VI) is removed to the hydrosphere, leaving behind an isotopically light "soil" Cr reservoir [1]. The operation of this process has been inferred, at least episodically, in the geological record back to 2.95 Ga [1], yet our understanding of Cr cycling in ancient weathering profiles and a view of temporal variations remain incomplete, with evidence for Cr oxidation appearing to contradict that available from Fe(II)/Fe(III) ratios in paleosols [2]. This study reports new Cr and Fe stable isotope and Fe(II)/Fe(III) data from the diabase-hosted ca. 2.45 Ga Cooper Lake paleosol, Ontario, Canada. Previous investigations of this paleosol interpreted it to have developed under reducing conditions [2-5] with major element patterns (loss of Mg, Fe, Na, Ca, addition of K) comparable to other pre-GOE mafic paleosols. Consistent with reducing conditions, an absence of Cr redox cycling during weathering is evident from homogeneous Cr/Al ratios and internally near-constant Cr isotope ratios. The Fe isotopic values, however, range between +0.169 to +0.492 $\infty \delta^{56/54}$ Fe_{IRMM014} and show a slight trend to heavier signatures upwards in the profile and with removal of Fe. Variation in Fe/Al ratios throughout the profile are confirmed to be controlled entirely by Fe(II) mobility and the shifts in $\delta^{56/54}$ Fe_{IRMM014} are interpreted to reflect mafic mineral dissolution during anoxic weathering processes. Accordingly, either the threshold of atmospheric O2 remained below the level required for Cr oxidation, in contrast to a Mesoarchean paleosol [1], oxidation was restricted to a now removed, upper horizon of the paleosol, or the local hydrological environment favoured water-saturated conditions during pedogenesis.

[1] Crowe, S.A., et al. (2013) Nature 501: 535-538.

[2] Rye, R., Holland, H.D. (1998) American Journal of Science 298: 612-672.

[3] Sreenivas, B., et al. (2008) Goldschmidt Conference Abstracts :A890

[4] Utsunomiya et al. (2003) Geochim. Cosmochim. Acta 67: 213-221.

[5] Sutton, S., Maynard, J.B. (1993) Can. J. Ear. Sci. 30: 60-76.

Multistage evolution of Coorg granulites, S. India – constraints on timescales of evolution

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Our aim is to use newly developed tools of diffusion chronometry [1] to constrain the timescales of sequences of High-T Archean processes. This can be used as fingerprints of Archean geodynamics. Here we report the results of detailed studies on one granulite sample from the Coorg Block, S. India. We identified the following sequence of events in an initially well annealed (at ~ 800°C) 2-pyroxene granulite (opx-cpx-plag-ilm): (1) Melt-infiltration that heated the rock to ~900 - 950 °C accompanied by the formation of garnets according to: Opx + Cpx + Pl = Grt1 + Qz at ~ 11 kbar. (2) Breakdown of Grt1 at ~ 850 °C according to: Grt1+Qz = Opx2 + Pl2. (3) Metasomatism by influx of a CO2 and K-bearing (? brine) fluid after further cooling and decompression that led to formation of phases like biotite, followed by their breakdown at ~ 650 °C, 8 kbar according to: Bt + Cpx + Pl + Qz = Grt2 + Kfs. Grossular rich Grt2 occurs as overgrowths on Grt1 as well as discrete, individual crystals and is associated with large calcite crystals. Compositional zoning formed by diffusion of Fe-Mg has been measured at Opx-Cpx, Grt-Opx, Grt-Cpx, Grt1-Grt2 and Grt-Bt contacts. These are being modelled currently to determine the actual cooling/decompression paths and the timescales over which the individual processes described above occurred.

[1] Bhowmik, S. and Chakraborty, S. (2017) EPSL 460: 171 – 179.

Elemental analyses of bulk carbonaceous chondrites with SF-ICP-MS

Braukmüller*, N., Wombacher, F., Münker, C. *Universität zu Köln, Institut für Geologie und Mineralogie, Greinstr. 4-6, 507674 Köln, Germany n.braukmueller@uni-koeln.de

A new method has been set up for the analyses of major and trace elements in carbonaceous chondrites. Following HF-HNO3 bomb digestion of 50 mg sample powder and the addition of an internal standard, samples are 2,000 and 10,000 fold diluted for trace and major element analyses, respectively. Sample and calibration solutions are introduced into the plasma of an ElementXR SF-ICP-MS using a PFA spray chamber and nebulizer. The sample set comprises >20 samples of C2, CI, CR, CM, CO, CV and CK chondrites. The CM chondrite group has been investigated in more detail. The comparison of falls with hot and cold desert finds of different degrees of weathering and aqueous alteration displays homogeneous bulk rock compositions, except for the hot desert find Jiblet Winselwan that shows an enrichment in HREE and weathering sensitive elements like U, Sr, Ba and Li [1]. The C2 chondrite Tagish Lake is chemically similar to samples of the CM group but less depleted in volatile elements [2] (Fig. 1). In general the depletion of volatile elements with 50% condensation temperatures < 750 K is indicative for each carbonaceous chondrite group and all elements show the same degree of depletion independent of the 50% condensation temperature (Fig. 1). This pattern likely results from two component mixing between refractory materials and a component of CI composition. Two samples deviate from that pattern (not shown). The Antarctic CI chondrite Y-980115 is severely depleted in Bi, In, Cd and TI relative to Ivuna, while EET 96026, which displays a CV chondrite like overall element pattern, shows a stronger depletion of all volatile elements with condensation temperatures lower than Cs (except Zn and Se). This volatile element loss may result from thermal alteration on the parent body [3].



Fig. 1: Abundance of volatile elements for different carbonaceous chondrite groups relative to CI. Elements have decreasing 50% condensation temperatures from left to right [4].

[1] Friend, P. et al. (2016) LPSC 47, #1893.; [2] Friedrich, J.M. et al. (2002) MAPS 37, 677-686.; [3] Chaumard,, N. et al. (2012) Icarus 220, 65-73.; [4] Lodders, K. (2003) Astrophys. J. 591, 1220-1247.

Early life driven by thermal forces in pores of rock?

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The Origin of Life is one of the fundamental, unsolved riddles of modern science. Life as we know it is a stunningly complex non-equilibrium process, keeping its entropy low against the second law of thermodynamics. It is straightforward to argue that first living systems had to start in a natural non-equilibrium setting. Arguing along a chain of experimental evidences [1-6] using non-equilibrium microsystems we suggest that geological temperature gradients across porous rock should be able to drive molecular evolution, i.e. the combined replication and selection of genetic molecules towards ever increasing complexity. We will give an overview over the progress and discuss how biology can emerge from geology along a line of experimentally testable hypothesis.

[1] Baaske, Weinert, Duhr, Lemke, Russell & Braun, PNAS 104, 9346–9351 (2007).

- [2] Mast, Schink, Gerland & Braun, PNAS 110, 8030-8035 (2013).
- [3] Mast & Braun, PRL 104, 188102 (2010).
- [4] Obermayer, Krammer, Braun & Gerland, PRL 107, 018101 (2011).
- [5] Kreysing, Keil, Lanzmich & Braun, Nature Chemistry 7, 203–208 (2015).
- [6] Matthias Morasch, Dieter Braun, and Christof B. Mast, Angewandte, doi: 10.1002/anie.201603779 (2016)

Constraints on metal mobilization in early Proterozoic marine sediments from Uranium isotopes Brüske, A.*, Schuth, S., Weyer, S.

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Uranium (U) is a redox-sensitive trace metal whose redox changes induce characteristic isotope fractionation. These signatures are preserved in the rock record and U isotopes may thus contribute to reconstruct the redox evolution of the early Earth atmosphere and oceans. Here we aim to apply this proxy on Archean and early Proterozoic sediment archives. First analyses of U isotopes in sediments from the Transvaal supergroup (Kapvaal craton, Duitschland and Timeball Hill formations, 2.368 - 2.486 Ga) that were deposited across (before and after) the Great Oxidation Event show significant authigenic U enrichment of 1 to 7 times average continental crust. All investigated samples origin from drill cores and most of them preserved $\delta 234/238U$ values around the secular equilibrium ($\delta 234/238U = 0 \pm 1 \%$), indicating negligible U mobilisation during sub-recent processes. Those samples with significant U enrichment (UEF > 2, relative to average continental crust) show $\delta 238/235U$ ranging between -0.8 ‰ to -0.1 ‰ (against CRM-112A), i.e. both isotopically heavier and lighter than average continental crust (\approx -0.3 ‰). These initial results confirm that oxygen levels in the atmosphere and/or uppermost ocean water column were already high enough, some 100 Ma before the GOE, to generate significant isotope fractionation during weathering-induced U mobilisation and subsequent deposition.

Novel iron nitrides synthesized at the conditions of the deep Earth's interiors

Bykov, M.*, Bykova, E., Glazyrin, K., Aprilis, G., Koemets, E., Chuvashova, I., Liermann, H.-P., Dubrovinsky, L. *Bayerisches Geoinstitut, University of Bayreuth, Universitaetsstrasse 30, D-95440 Bayreuth, Germany maxim.bykov@uni-bayreuth.de

The amount of nitrogen in iron meteorites indicates that significant quantities of nitrogen (about 0.5 wt %) could have been incorporated in Earth's core during accretion. Since iron meteorites are derived from the core material of differentiated bodies in the early solar system, nitrogen is likely a component of the light alloying elements in the Earth's core [1]. However, the phase relations in Fe-N system at high-pressure high-temperature conditions are not well studied to date. We have investigated the chemical relations in Fe-N system using single-crystal X-ray diffraction in laser-heated diamond anvil cells. We have discovered four novel iron nitrides with compositions Fe3N2, FeN, FeN2 and FeN4. Our results suggest that higher pressure favors formation of iron nitrides with higher nitrogen content (Fe3N2 \rightarrow FeN4). In this contribution, the phase relations in the Fe-N system and possible implications for the Earth's core will be discussed.

[1] Adler, J. & Williams, Q (2005) J. Geophys. Res. 110, B01203.

Where geo- meets astrobiology: Tackling the origin of organic matter on early Earth

Duda*, J.-P., Thiel, V., Bach, W., Bauersachs, T., Mißbach, H., Reinhardt, M., Schäfer, N., Van Kranendonk, M.J., Reitner, J.

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Tracing the earliest life on Earth is one of the most challenging endeavors of current geo- and astrobiological research. Given that all extant life on Earth is based on carbon, organic matter in ancient rocks may provide evidence of its presence in the deep past. However, the origin of organic matter preserved in the oldest rocks on Earth is still enigmatic: Does it represent an unambiguous fingerprint of life or is it, partly at least, derived from abiotic sources (e.g. extra-terrestrial delivery, hydrothermal synthesis)? We tackle this question by analyzing organic matter in a variety of early Archean environments from the Pilbara Craton (Western Australia) and in selected younger analogue systems. Our observations suggest that a large proportion of the early Archean organic matter was indeed biologically produced – a finding that is supported by experimental data obtained via maturation of extant biomass and the synthesis of abiotic organic matter via Fischer-Tropsch-like processes. The results underline the existence of a complex interplay between biological and abiological processes in Archean environments, and contribute to our understanding on how Earth became a habitable place. Furthermore, our studies have important implications for the identification of organic biosignatures on Earth and, potentially, beyond.

Exhumation of deep crustal granulites during Neoarchean terrane accretion in the Nuuk region, SW Greenland.

Dziggel*, A., Kokfelt, T.F., Kolb, J., Kisters, A.F.M., Reifenröther, R. * Institute of Mineralogy and Economic Geology, RWTH Aachen University, Wüllnerstraße 2, 52062 Aachen adziggel@emr.rwth-aachen.de

Terrane accretion in the Nuuk region shares many characteristics with modern accretionary systems, including the strong evidence for regional-scale crustal thickening and presence of different thermal regimes and PT paths. Crustal convergence resulted in the collision of the Færingehavn terrane (FT) with the Tre Brødre and Tasiusarsuaq terranes (TT) [1]. The TT exposes a deeply eroded section through the upper plate, made up of granulite and amphibolite. In its centre, nappes of deep crustal granulites (800-950°C, 9-12 kbar) were exhumed into mid crustal levels during NW-vergent thrusting at ca. 2.75-2.72 Ga, coeval with underthrusting of the FT. The presence of abundant leucosomes and syntectonic pegmatites point to a rheologically weak crust in which nappe emplacement was assisted and/or triggered by partial melting. We propose that the emplacement of deep crustal granulites occurred in direct response to crustal convergence and final collision of the terranes at ca. 2.72-2.70 Ga.

[1] Dziggel, A. et al. (2014) Prec.Res. 242, 22–38.

Ruthenium isotopic evidence for an inner solar system origin of the late veneer

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Excess abundances of highly siderophile elements (HSE) in the Earth's mantle are commonly interpreted to reflect the addition of a late veneer comprised of primitive meteoritic material after core formation had ceased. The late veneer either represents a left over population of objects remaining in the terrestrial planet region after Earth's accretion [1], or derives from more distant asteroidal [2] or cometary [3] sources. Distinguishing between these origins is important because a late veneer consisting of carbonaceous chondrites could be the principle source of the Earth's volatiles and water [2]. Until now, however, it was not possible to establish or rule out a genetic link between the late veneer and such volatile-rich materials. Such links can be determined using Ru isotopes, because the Ru in the Earth's mantle predominantly derives from the late veneer [4], and because meteorites exhibit Ru isotope variations reflecting the heterogeneous distribution of stellar derived dust [5-7]. To address this issue we have obtained Ru isotopic data for a comprehensive set of chondrites and two terrestrial chromitites. The Ru isotope composition of the chromitites is indistinguishable from the Ru solution standard, suggesting that their composition is representative for the Earth's mantle. Compared to the Earth's mantle all analyzed chondrites display resolved nucleosynthetic Ru isotope anomalies reflecting variable deficits in s-process Ru nuclides. The Ru isotopic anomalies are most pronounced for ϵ^{100} Ru (the parts per 10,000 deviation of the ¹⁰⁰Ru/¹⁰¹Ru from the terrestrial standard value). The magnitude of nucleosynthetic ϵ^{100} Ru anomalies scales with increasing heliocentric distance (terrestrial<enstatite<ordinary<carbonaceous) [7]. Highly reduced and dry inner solar system materials like enstatite chondrites have Ru isotope compositions most similar to Earth (ϵ^{100} Ru=-0.08±0.04), whereas oxidized and volatile-rich carbonaceous chondrites are most different from terrestrial (ϵ^{100} Ru up to -1.4). These data, therefore, suggest that materials from the outer solar system, such as comets, also have a strong deficit in s-process Ru, similar to or even larger than observed for carbonaceous chondrites. Therefore, the large Ru isotope anomalies documented for carbonaceous chondrites indicate that the late veneer cannot be comprised of such volatile-rich outer solar system materials, implying only a minor role of the late veneer for the delivery of Earth's volatiles. Even if as recently proposed, only about 60% of the Ru in the Earth's mantle was added by the late veneer [8], a late veneer of carbonaceous chondrites can still be excluded because it would have a large deficit in s-process Ru with ϵ^{100} Ru \approx -1, as typically observed for carbonaceous chondrites. This would have to be balanced by an s-process enriched Ru isotopic composition of the Earth's pre-late veneer mantle with ε¹⁰⁰Ru≈+1. However, such a large s-process enriched composition for the Earth's pre-late veneer mantle is unlikely given that the Earth's isotopic composition for several elements (Ca, Ti, Ni, Cr, O) is similar to enstatite chondrites [9]. Because these elements record the Earth's entire accretion history this similarity, therefore, indicates that on average the terrestrial building blocks were isotopically most similar to enstatite chondrites [9]. Hence, any reasonable Ru isotopic composition of Earth before the late veneer should be close to enstatite chondrites (ϵ^{100} Ru=-0.08±0.04). While our Ru isotope data refute a late veneer comprised of carbonaceous chondrites, the abundances and isotopic compositions of hydrogen, carbon and nitrogen in the Earth's mantle indicate that the Earth's volatiles most likely derive from carbonaceous chondrite-like material [10]. This requirement can be relaxed if carbonaceous chondrite-like objects were scattered into the inner solar system early in the Earth's accretion, as predicted by recent dynamical models [11]. These bodies would have been probably characterized by a deficit in s-process Ru compared to the present day Earth's mantle, but because this material was added during the main stages of accretion and core formation this Ru would have been quantitatively removed to the Earth's core and would have not affected the Ru isotopic composition of the Earth's mantle. Thus, our Ru isotopic data are consistent with the accretion of volatile-rich bodies from the outer solar system during the main stages of the Earth's growth, but not during late accretion.

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Algal bloom in a Paleoproterozoic pegmatite from Volyn, Ukraine - an example of geo-bio-interaction in the early Earth history

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We investigated organic matter (OM), which was found in the pegmatite district of the Volodarsk-Volynskii, Zhytomyr Oblast in NW Ukraine. The pegmatites are genetically and spatially connected with rapakivi-like differentiated granites of the gabbro-anorthosite Korosten pluton with an intrusion age of 1.8-1.76 Ga. OM occurs in different forms: As carbohydrates in fluid inclusions in beryl; as carbohydrates in brown opal; as ammonia in buddingtonite and tobelite; as C-H-N dominated material, which is enriched in Zr, REE, Th, U, and other high-field-strength elements; as fossil algae material termed "kerite" from miarolitic open chambers. Stable isotope data of buddingtonite, brown opal and kerite clearly indicate the biogenic origin of OM.

Buddingtonite-tobelite-OM-brown opal were identified in a pseudomorph after beryl in a breccia. The breccia formation is considered as a late-stage event after cooling of the pegmatite to $T \le 200^{\circ}$ C, possibly due to fluid overpressure of the large miarolitic chambers with a volume of 40 m³, in extreme cases up to 250 m³. The pseudomorph after beryl is situated in a matrix of opal-chalcedony with small fragments of albite, alkalifeldspar and quartz, and consists of a rim rich in bertrandite, an inner zone of dominantly buddingtonite + F-bearing muscovite + opal ± betrandite ± euclase ± organic matter ± Ta-oxide ± REE-minerals, with a core of Fe-rich muscovite + smectite ± chlorite. Buddingtonite solid solutions of NH₄-K-H₃O occur as euhedral, platy crystals with typical sector zoning and as fibrous crystals, replacing alkalifeldspar. F-bearing muscovite has a minor but significant tobelite component. Kerite is hair-like fibrous organic matter interpreted as fossil algae (1, 2) grown in the miarolitic chambers. Scanning electron microscopy shows fibres with a diameter of ~3 µm thickness, several mm long, with a smooth surface and typical branching. Broken fibers show a hollow core a few nm wide and some indications of cell walls.

Buddingtonite formation requires a high concentration of NH₄ in a fluid and is therefore only possible in Earth history, once enough organic matter is present. We propose a model for the evolution of the pegmatite and the buddingtonite formation, which starts with pegmatite intrusion into a near-surface environment rich in organic matter. Algae bloom produced kerite in the pegmatite chambers. Hydrothermal convection cells mobilized organic matter, mixed it with the igneous fluid and incorporated it into the pegmatite, concentrating high field strength elements in the organic matter, and causing the breakdown of beryl to buddingtonite+bertrandite. During further cooling, the chambers were destroyed, the high amount of Si precipitated as opal, and F-muscovite partly transformed into tobelite. Such a scenario is only possible once significant biogenic activity occurred in the late Paleoproterozoic. Buddingtonite commonly forms in hydrothermal deposits via interaction of NH₄-bearing fluids of biogenic origin, and therefore most localities are known from Phanerozoic rocks. To our knowledge this is the oldest reported locality of buddingtonite.

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Petrology, geochemistry and age of the syn-Moodies Lomati River Sill in the Barberton Greenstone Belt

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The doleritic Lomati River Sill (LRS) in the central BGB is a unique elongate body just north of the major Inyoka Fault (IF). The LRS extends for ~10 km NE-SW, is 50-500 m wide and is embedded in folded volcaniclastics of the upper Fig Tree Group (~3225 Ma). Primary mineral phases occur as relicts only. Whole-rock main and trace element geochemistry indicate an internal zonation (MgO: 5-14 %, Cr: 15-650 ppm, Ni: 70-230 ppm, (La/Sm)_N: 1-4). U-Pb single-zircon ages of 3211±18 Ma are interpreted as time of intrusion, ages of 3180±11 Ma as alteration. These ages overlap with (1) a peperitic stockwork in Moodies Group sediments (3208±13 Ma) south of the IF, and (2) a tholeiitic basalt widespread in Moodies strata throughout the BGB (~3220±3Ma) Petrography, geochemistry, map relationships and ages all indicate a close genetic relationship between sill intrusion, stockwork formation, volcanism and contemporaneous basin collapse.

Effect of geologically-constrained environmental variables on the atmosphere and biosphere of early Earth

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The Great Oxidation Event (GOE) marked a spectacular rise of molecular oxygen in the history of Earth enabling wideranging habitability and allowing complex life to develop. Recent advances constrain environmental conditions such as e.g. atmospheric composition, surface pressure and ocean temperature from geological records. We have updated the longwave radiation scheme of our newly developed Coupled Atmosphere Biogeochemistry (CAB) Model [1] with the more flexible MRAC scheme [2] in order to be able to simulate a much wider range of pressure and temperature implied by geological data. With this updated model version we will perform model scenarios for three periods, namely before, during and after the GOE and examine what effect the new results have for our understanding of the atmosphere and biosphere of early Earth.

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Oxidative photosynthesis before the Great Oxygenation Event.

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Cyanobacteria are thought to have evolved under freshwater conditions, with their transition into oceans marking large scale oxygenation of the atmosphere toward the end of the Archean. Our study assessed the ability of modern day descendants of the oldest cyanobacteria, to survive in briny or modern day sea water. Gloeobacter violaceus and Cylindrospermopsis thermalis were cultured in media analogous to fresh water, sea water and briny water under present atmospheric conditions (PAL) and reduced O2 elevated CO2 (rO2eCO2; 600:2000 ppm) conditions. Cultures were assessed for their photosynthetic efficiencies under PAL and rO2eCO2. The production of extracellular polymeric substances (EPS) and respiration activity was assessed using fluorescent microscopy. Oxygen production and REDOX stress levels were determined on cultures grown on quartz sand under similar growth conditions. Results: The nett photosynthesis rate (NP) increased significantly in all cultures when assessed under rO2eCO2. While unable to survive the transition to full sea salt strength media, G. violaceus was able to grow in half-strength sea salt or briny culture media. Artificial mats grown under rO2eCO2 atmosphere showed clear, localised peaks of O2 production with a concomitant increase in REDOX levels in the immediate surrounding media. Conclusion: This study supports the proposal that early cyanobacterial species would have been able to grow in increasingly salty water, allowing for the transition to the open ocean growing blooms necessary for the large scale oxygenation of the atmosphere. The increased O2 levels in the media of cultures grown under rO2 eCO2 demonstrates that submerged cyanobacteria would have had a long time to gradually evolve to cope with the stress of elevated O2 levels, prior to the GOE. This is supported by the increased exposure to O2 and REDOX stresses measured in the subaerial pseudomats we generated in the laboratory. Future work: Nitrogen is essential for all life on Earth. Abiotic N sources were not enough to support large scale biological growth during the Archean, supporting the early evolution of N fixation. N fixation activity based on Mo was identified in the last common ancestor (LUCA), supporting its activity during the Archean. The experimental culture system developed in our current project will allow us to investigate the potential limitations on N fixation under conditions prevailing during the Archean in the ocean, freshwater lakes and hotspring environments.

Indigenous and non-indigenous Precambrian hydrocarbons: what information can we extract about Earth's earliest biota?

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For many years the hydrocarbon remnants of diagnostic bacterial and eukaryotic membrane lipids (i.e. so-called biomarkers or fossil lipids) preserved in Archean sedimentary rocks have been used to reconstruct the nature and diversity of Earth's earliest biosphere (e.g. Brocks et al., 2003). An increasing awareness of contamination problems (e.g. Rasmussen et al., 2008) led us to scrutinize these data: in 2012 an ultra-clean drilling operation was undertaken to recover some of the oldest sedimentary rocks on Earth that may still harbor diagnostic biomarker molecules in an unprecedentedly clean manner. The results revealed a molecular organic inventory composed of short and stable molecules indicative of a high thermal overprint, yet devoid of any diagnostic polycyclic terpenoids (French et al., 2015). This outcome shows that even the best-preserved Archean rocks are too thermally mature to harbor molecular information on past biota in the form of currently known proxies. The implications for early life studies are two-fold: for one we must try to find and target progressively younger and thermally better-preserved sedimentary sequences; secondly, we must explore the existence or recognition of novel, or rather alternate, molecular markers with remnant biological diagnosticity yet a higher threshold to thermal destruction. In this presentation I will discuss the current state of knowledge on indigenous and syngenetic, indigenous and non-syngenetic, as well as nonindigenous hydrocarbons found in Archean rocks. An overview will be given on our achievements in recognizing contamination (e.g. Leider et al., 2016), our current knowledge on the Proterozoic record of certainly-indigenous biomarkers (unpublished), as well as how our group is exploring pathways to maximizing the information-exploit of thermally mature Archean rocks in order to potentially still gain some traces of knowledge on Earth's earliest biosphere.

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Evolution of a bumpy core-mantle boundary from a chemically stratified mantle

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There is much evidence that the core mantle boundary does not resemble the picture of a simple thermal boundary layer, as known from thermal convection at high Rayleigh number. Rather it seems to be of complex structure, possibly induced by compositionally dense material. Present models of mantle convection, aiming at simulating the complex structure and dynamics of the lower boundary layer require several ad hoc assumptions. Most of them postulate the presence of a sufficiently dense layer at the transition from the magma ocean state to solid state mantle convection. Especially the density excess distinct material needs to be assumed. Both conditions are critical for the dynamics in a sense, that too much, too dense material results in a 'pancake-shaped ' flat layer without any topography while for having too little, not sufficiently dense material, thermal convection would simply sponge off the distinct material. Unfortunately the values of excess density and mass can hardly be constrained .Further it seems unlikely that conditions at the end of the magma ocean epoch resembled a chemically homogeneous mantle From a series of model calculations, starting out from an initial mantle as possibly evolve by fractional crystallization, all with realistic rheology, we find that chemical transport across the CMB plays a key role for the formation of a bumpy boundary...Parameterizing the chemical transport by diffusion with an extreme low diffusivity, leads selfconsistently (without assuming any preexisiting dense material) to the formation of compositional piles with different degrees of complexity. Dense material, slowly entering the mantle is accumulated by thermal advection and thus piles are formed. At the same time the presence of the piles reduces further compositional influx. We find the presence of such piles to significantly influence the thermal - and compositional evolution of the mantle system .

A Paleoarchean coastal oxygen oasis, Moodies Group, Barberton Greenstone Belt

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Thick tidal-facies photosynthetic biomats in the Moodies Group of the BGB (3.22 Ga) are adjoined landward by coastalfloodplain aridisols in which abundant gypsum concretions formed in the vadose zone, and seaward by thick prodelta deposits with BIF, jaspilites, and magnetic shales. Early widepread silicification prevented excessive compaction, limited fluid alteration of primary minerals, and preserved a plethora of sedimentary structures. The oxide facies (sulfates and Fe-oxides, respectively) framing the tidal biomats document a large-scale "oxygen oasis"-type ecosystem along an extensive Paleoarchean shoreline and lend support to the early and prolonged oxygenation of planet Earth. The presence of updip sulfate reducers and downdip potential photoferrotrophs demonstrates the early establishment of complex, interrelated microbial ecosystems related to the tectonic consolidation of stable shallow-water settings.

A geodynamic model for the lower Onverwacht Group, Barberton Greenstone Belt (South Africa)

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We report majorand trace element as well as whole-rock Hf-Nd isotope data for rocks of the lower Onverwacht Group of the Barberton Greenstone Belt (BGB). Using the acquired data in combination with previously published results, a consistent model for the petrogenesis of the lower Onverwacht Group volcanic sequences (Sandspruit, Theespruit, Komati Fms.) is presented. Based on melting and mixing models, we propose that some of the Sandspruit and Theespruit volcanic rocks were contaminated by magma mixing with felsic volcanic melts. Others were the product of fractional crystallization of komatiite melts in layered complexes as they are found in the BGB. We interpret the Komati Fm. komatiites as melts resulting from extensive lithospheric mantle cannibalism triggered by hot asthenospherederived melts.

Search for palaeoatmospheric noble gas isotopes

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Palaeoatmospheric noble gas isotopes can be useful tracers for describing the terrestrial crust-mantle system in the past. In addition, they may further constrain the volatile degassing history of the solid Earth and constrain potential loss processes from the atmosphere into space. For example, a major source of production of 40Ar* from decay of 40K (half-life 1.25 Ga) is the continental crust. Hence, the proportion of stable crustal blocks and the degassing efficiency of Ar from its source rocks are strongly related to the evolving 40Ar/36Ar-ratio of the atmospheric system, which includes hydrosphere and cryosphere [1]. 36Ar is a primordial isotope and its abundance in the atmosphere commonly is considered to be the result of nearly complete (>95%) and very early mantle degassing, possibly related to giant impact events in early Earth history.

Major obstacles of deciphering an ancient atmospheric component are contributions of crustal fluids entering a rock via interaction during metamorphic or diagenetic processing, in situ radiogenic contributions and eventually, contributions from modern atmospheric gases. Furthermore, the most suited lithologies which should have formed in contact with atmospheric gases (including interaction with seawater) are commonly fine grained (e.g. shales, biogenic matter) or are expected to be less retentive for noble gases (e.g. carbonates). Current research has focussed on chert / quartz and barite. Only one study [2] of an Archean quartz reported a 40Ar/36Ar-ratio of 143 ± 24 at 3.5 Ga or 211 ± 21 at 2.7 Ga depending on the exact sample age, which is significantly lower than at present (40Ar/36Ar = 296). Further information comes from the study of Xe, because the composition of primordial xenon isotopes of the present atmosphere is non-chondritic. The composition of xenon in Archean barite has led to speculations that the atmospheric xenon composition was initially chondritic, and since then has been altered by ionisation-induced isotope fractionation and loss processes in the uppermost atmosphere [3]. However, both reported argon and xenon isotopic anomalies are a consequence of decay corrections for 40Ar* and 130Xe* (from 130Ba-decay) ([2], [3]), and a certain assumption regarding the 130Ba-decay constant, whereas the uncorrected data show no significant deviation from modern atmosphere. Hence, both studies [2, 3] cannot fully exclude a late isotopic re-equilibration with modern atmospheric gases.

Apparently, our knowledge of the palaeoatmospheric noble gas record is still limited. We have started with a more extended investigation utilizing different minerals and different lithologies of various epochs. In a first step we analyse the noble gas composition of a variety of minerals and rocks (e.g. quartz / chert, barite, carbonates) by stepwise crushing in order to characterise their crustal fluid budget and to check for potential atmospheric remnants. Under favorable circumstances mixing relations will allow for calculation of atmospheric 40Ar/36Ar-ratios. For example, a linear correlation between 40Ar/36Ar- and 4He/36Ar-ratios has been found to define an atmospheric 40Ar/36Ar-ratio of about 235±154 in Transvaal dolomite, South Africa (age: 2.4-2.5 Ga [4]). In spite of the still poor precision this result demonstrates the potential of a multi-isotope and –element study for deconvolution of palaeoatmospheric compositions. It is also intended to prepare separates of less common minerals, e.g. pyrite, magnetite / hematite. However, for these minerals grain sizes are a limiting factor that may require application of in situ methods. Furthermore, we plan analyses of neutron-irradiated aliquots from promising samples measured within the first (non-irradiated) series, utilizing the production of 38Ar from chlorine by reactions with thermal neutrons. It is thus potentially possible to distinguish between saline and non-saline fluid inclusions, with the latter more likely reflecting entrapment under ambient atmospheric conditions (e.g. [2]). In addition, this method may allow simultaneously constraining the age of our samples.

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First geochronologically-resolved Meso-Archean O2 production

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Several lines of evidence suggest that oxygenic pho-tosynthesis predated the oxygenation of the atmos-phere by several 100 million years. However, geo-chemical signals for pre-GOE oxygen production have mostly been found in deep-marine sediments [1]. Their link to photosynthetic activity at the Earth's surface remains tenuous and none of these signals have been validated as syngenetic. Here we present rare earth element data for shallow-water banded iron formation from the 3.2 Ga Moodies Group, Bar-berton Greenstone Belt, that carry a clear signal for Ce oxidation (Ce/Ce*PAAS down to 0.2). Sm-Nd geo-chronology shows closure of the REE system at 3.14 Ga +/- 200 Ma, firmly establishing O2 production at ca. 3.2 Ga. Our data link shallow-water BIF precipita-tion with nearby tidal-zone biomats in the same stratigraphic unit, providing a clear genetic model for early O2 production. Our findings provide unambiguous and geochronologically-resolved evidence that oxygenic photosynthesis flourished 3.2 Ga ago.

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The Godthåbsfjord gold province in the North Atlantic craton of southern West Greenland Kolb*, J., Lebrun, E., Thébaud, N., Dziggel, A., Fiorentini, M.

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Orogenic gold deposits are an integral part of Archean granite-greenstone belts [1]. The hypozonal, high-temperature class of these deposits appears to be restricted to early Earth evolution [2]. The Godthåbsfjord gold province in southern West Greenland, close to the capital Nuuk, hosts a number of hypozonal orogenic gold occurrences. The wall rocks range from Eoarchean orthogneiss to Neoarchean mafic granulite, amphibolite and aluminous gneiss. The orogenic gold mineralization formed between ca. 2660 and 2600 Ma, approx. 40–100 m.y. after terrane assembly and peak metamorphism, during retrograde exhumation. Gold mineralization is associated with hydrothermal alteration at 530-630°C and 4-6 kbar. The hydrothermal system was likely triggered by orogenic processes to the east that initiated tectonic reactivation and rehydration of its foreland.

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Were early Archaean greenstone belt remnants in the eastern Kaapvaal craton, southern Africa, part of a large continental plateau basalt province?

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We are testing the hypothesis that the Barberton Greenstone Belt (BGB) and several greenstone remnants in western Swaziland and northern KwaZulu-Natal Province of South Africa were once part of an extensive early Archaean continental flood basalt sequence covering a large part of the southeastern Kaapvaal craton. We are testing the hypothesis that the Barberton Greenstone Belt (BGB) and several greenstone remnants in western Swaziland and northern KwaZulu-Natal Province of South Africa were once part of an extensive early Archaean continental flood basalt sequence covering a large part of the southeastern Kaapvaal craton. There is increasing evidence that the oldest sequence of the BGB, the Onverwacht Group (ca. 3.55-3.40 Ga), was deposited on older continental crust as seen in rare zircon xenocrysts, whole-rock Lu-Hf isotopes and Hf-in-zircon isotopic data. Greenstone remnants in northern and southwestern Swaziland (BGB, Dwalile, Mankayane, Sicunusa) contain felsic rocks, all with similar zircon ages of ca. 3.45 Ga, and all experienced metamorphic overprinting and deformation at ca. 3.2 Ga, resulting in obliteration of the original contact relationships and infolding with granitoid gneisses. The southernmost greenstone remnant, the Nondweni Greenstone Belt, has zircon ages of 3.53-3.41 Ga [1]. All of the above greenstone sequences as well as undated greenstone remnants near Piet Retief contain bimodal komatiite-basalt and dacite-rhyolite volcanic associations typically found in more recent continental flood basalt provinces. We speculate that the above greenstone sequences neither represent early Archaean ocean floor nor island arc environments but were originally floored by TTG-dominated older continental crust, and constituted a large flood basalt sequence, similar to what has been proposed for the early Archaan greenstones in the eastern Pilbara craton of northwestern Australia [2].

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Diagnosticity of steroidal breakdown products in pyrolysates

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The thermal decomposition of lipid biomarkers that accompanies deep sedimentary burial has obscured the detection of early life traces in the Precambrian sedimentary record (e.g. 1). This is especially true for the Archean Eon, as recently revealed by ultra-clean drilling efforts (2). While intense molecular cracking results in the production of increasingly smaller fragments that cannot longer be attributed to a source specific precursor molecule (e.g. 3), specific degradation products of hopanes and steranes might however still carry diagnostic value for the reconstruction of past biota when found in mature sediment extracts. Previous pyrolysis studies analysing the thermal stability of kerogens and authentic biomarker standards have shown some characteristic alteration products (e.g. 4, 5) but it is not known if these compounds are unique to their precursors, or if they occur in nature. We have investigated this question with controlled heating experiments using 5¹/₂-cholestane as a representative eukaryotic biomarker under different reaction times and in the presence of different solid materials (kaolinite, montmorillonite, carbonate, activated carbon).

During pyrolysis in sealed glass tubes 5^[2]-cholestane undergoes decomposition into sterenes and derivatives of dimethylperhydrophenanthrene (DMPHPs) under conditions sufficiently severe to cleave carbon-carbon bonds of *n*-alkanes as previously reported (e.g. 6). Increased heating time and the addition of CaCO₃ lead to an increase in the abundance of DMPHPs compared to other cholestane-derived fragments, while DMPHPs are absent during pyrolysis in the presence of clays and activated carbon. However, the occurrence of DMPHPs has never been reported from natural rock extract and/or crude oils hitherto. A preliminary survey of a series of thermally mature Phanerozoic crude oils showed elevated abundances of androstane, pregnane and the presence of DMPHP in carbonate sourced petroleum, but not in shale-derived petroleum of similar thermal maturity. This agreement between laboratory experiments and natural samples indicate that DMPHP can likely be used as a eukaryotic marker in fluids too mature to have preserved intact alkylated steranes. Such data might open a new analytical window for molecular geobiological approaches to basins that were hitherto precluded by their elevated thermal maturity.

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LA-ICP-MS zircon ages for clastic sediments of the Moodies Group, Barberton Greenstone Belt, South Africa and Swaziland

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We have undertaken LA-ICP-MS dating of zircons separated from sandstones of the Moodies Group, Barberton Greenstone Belt (BGB), South Africa and Swaziland, as part of a pilot study, using a using an Agilent 7500ce quadrupole inductively-coupled mass spectrometer coupled to an ESI NWR193 ArF excimer laser system with 193 nm wavelength at the University of Mainz. The Moodies Group is the youngest lithostratigraphic sequence in the BGB with a depositional age of ca. 3220 Ma [1]. It contains quartz-rich sandstones and rare conglomerates with rare granitic clasts of granite of unknown origin (documented from one location only) aside from abundant intra-greenstone belt lithologies. Four samples come from a single stratigraphically continuous succession in the Stolzburg Syncline, ca. 1500 to 2000 m thick; the other samples represents different locations in the basal Moodies. Two samples were collected from the Swazi BGB.

The zircons were mounted in epoxy resin and were analyzed together with zircon standards GJ1 and 91500. No correction for common Pb was made so far. Many analyses are discordant, and some are reversely discordant, which may partly be due to Pb-loss at unspecified times in the past and/or non-correction for common Pb. We therefore only consider concordant and near-concordant data.

Samples 12-003 and 12-007 represent the basal Moodies Group in the Stolzburg Syncline. 12-003 contains one concordant zircon at ca. 3500 Ma and one slightly reversely discordant grain of about the same age. 12-007 contains several grains around 3300 Ma in age whereas two significantly reversely discordant grains could potentially be as old as ca. 3600 Ma, but their reverse discordancy is suspect. The remaining samples from the Stolzburg Syncline yielded a large number of discordant analyses, but one gran in 14-004 and one grain in 16-305 suggest ages close to 3600 Ma. One concordant analysis at ca. 1800 Ma in 16-303 is anomalous and may reflect a thermal event in the BGB area represented by mafic dykes. The two samples from Swaziland display similar age patterns but contain no zircons older than ca. 3450 Ma. Two reversely discordant results could potentially represent slightly older grains.

If the zircon age spectra reflect unroofing in the BGB and surrounding areas the stratigraphically youngest sample should contain the oldest zircons, whereas ages in the basal Moodies samples should be younger. This is not the case in our age spectra. In fact the oldest reliable concordant SHRIMP zircon age for the basal Moodies conglomerate is from a large granite clast at the Ezzy's Pass locality with a ²⁰⁷Pb/²⁰⁷Pb age of 3570±6 Ma [2].

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Characterization of Nitrogen-bearing phases in Enstatite Chondrites

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Several isotope systems (O, Ca, Ti, Cr, Ni, Mo, Ru) suggest enstatite chondrites (ECs) as best analogue material for the building blocks of the Earth [e.g., 1,2,3]. Investigation of N-bearing phases in the ECs yields information on the components that comprised the starting inventory of terrestrial nitrogen. Ti- and Si-nitrides and Si2N2O are generally assumed to be the major N-carriers in ECs, which typically contain several 100 ppm N. Si3N4 grains were identified by SEM-EDS in a set of ECs of petrologic types 3-4. Subsequent investigation by NanoSIMS showed an average δ 15N of (– 61 ± 1 ‰) (Fig. 1), lighter than both reported N-isotopic compositions for bulk ECs (–24 ‰) [4] and Si2N2O (–18±3 ‰) [e.g., 5], but heavier than the inferred compositions of the Sun and the protosolar nebula [6]. TEM investigation revealed two grains to be polycrystalline, indicating formation by condensation from the Solar Nebula and not by exsolution from the host material. We estimate bulk abundances of ≤10 ppm for Si3N4, while Si2N2O and TiN are virtually absent in the samples. This observation is in contrast to the general assumption made for the Nitrogen-carriers in ECs. Other N-bearing components are organic material (OM) and graphite. However, OM contains only a minor part of the total N (4-24 ppm, [7]), with δ 15N typically $\mathbb{Z}0$ ‰ [7]. Graphite abundances in ECs are 400 ppm on average [8], and reported N concentrations in graphite from St. Marks (EH5) are <3,600 ppm [9]. Based on this limited data set, we calculate that less than 2 ppm of the several 100 ppm nitrogen in the bulk ECs is hosted in the graphite. Thus, the major fraction of N has to be contained in other phases, with Fe,Ni metal or sulfides as the most likely candidates.



Figure 1. C-& N-isotopic compositions of 277 Si3N4 grains from PCA 91020 (260 grains), MAC 88136 (8 grains), Kota-Kota (8 grains), and Indarch (1 grain). The white cross symbol represents the weighted average for all grains from this study, and the blue line denotes the average δ 15N for bulk ECs (-24 ‰). Reference data are from [10]. The black dotted lines denote the terrestrial standard value. All errors are 1o.

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Constraining the Parameter Space for the Solar Nebula

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What were the physical conditions in the Solar Nebula which allowed the formation of planets, especially the formation of the Earth? It is believed that planets are formed by so-called planetesimals, objects being bound by their own gravitational attraction rather than surface and material binding forces. In the early stage of planet formation dust grains grow to pebble size. These pebbles drift and may get trapped in pressure bumps and form planetesimals after gravitational collapse. The outcome of the spatial planetesimal distribution within a protoplanetary disk depends on the disk properties such as the level of turbulence, the initial disk mass, or the size of the disk. We used a sophisticated model where planetesimal formation directly depends on the pebble flux. This allows to exclude certain parameters by comparing the initial planetesimal distribution with constraints from other works.

Effect of planetary rotation on the differentiation of a terrestrial magma ocean Maas*, C., Hansen, U. *WWU Münster, Institute for Geophysics, Corrensstraße 24, 48149 Münster, Germany christian.maas@uni-muenster.de

The crystallization of a terrestrial magma ocean is of key importance for the chemical structure of the Earth, the mantle evolution and the onset of plate tectonics. During the magma ocean phase, the Earth rotated very fast with a period between two and five hours. Due to this fast rotation and the small magma viscosity, rotation probably had a profound effect on the early differentiation of the Earth. We investigate the influence of planetary rotation on magma ocean dynamics using a spherical shell model. Depending on the strength of rotation, crystals accumulate at mid-latitude between pole and equator or at the equator. At high rotation rates, jet-like motions in longitudinal direction that have different directions on the northern and southern hemisphere dominate the dynamics of fluid and crystals. Overall, first numerical experiments show that the crystal distribution crucially depends on latitude, rotational strength and crystal density.

Vortex Formation through hydrodynamic instabilities

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How do dust grains grow to planetesimals? Dust grains are known to collide and stick together, but at a size of a few cm, their growth is limited by (1) their increasing relative velocity with size, leading to i.e. fragmentation; (2) drift motions, which move particles inward faster than the can grow, and (3) colliding particles may bounce off each other. To allow growth beyond this size, many mechanisms have been suggested, each of them in need of special environmental conditions, i.e. a trap formed inside the proto-planetary disk to bring enough grains together. To find such traps, we performed full 3D numerical simulations of protoplanetary disks with a negative temperature and entropy gradient and short to moderate cooling times. These conditions lead to the development of Vertical Shear Instability and Convective Overstability. We found that both instability mechanisms can form particle traps in the form of vortices. We show that the size and lifetime of the formed vortices is long enough to enable planetesimal growth.

Fiji: Probe of ancient continental growth?

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The debate whether Archaean continental crust and its TTGs (tonalite-trondhjemite-granodiorite series) are produced in a subduction-related setting or through partial melting of thickened oceanic crust is still not settled and will remain contentious. Furthermore, an open question is, if "Archaean" conditions for TTG generation still operate on modern Earth. Generally, the proportion of plagiogranitic rocks in modern oceanic crusts never exceeds 1 vol.%. Recent seismic surveys at the Izu-Bonin-Mariana arc [1] and Lau ridge [2] suggest a granitic composed middle crust comprising up to 25 vol.% of the crustal volume.

In order to estimate the significance of modern plagiogranites in arc-systems as putative equivalents to Archaean TTGs, we performed combined conventional trace element, high precision HFSE and Hf-Nd-Sr isotope measurements from various plutons from Viti Levu, Fiji. The plagiogranites exhibit geochemical variabilities in major and trace elements between and within plutons. Three different groups of felsic rocks can be distinguished by their ranges in K₂O and REE, the latter exhibit both LREE depleted and continental crust-like enriched patterns. No slab fluids or melts are required in order to produce the REE-enriched melts.

Based on our results, we can divide the Fiji tonalites into two distinct groups derived by fractional crystallisation of tholeiitic and island-arc tholeiitic melts, and one group of Med-K tonalites produced by dehydration melting of lower oceanic crust, showing distinct characteristics of Archaean TTGs.

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Surface reactivity of the anaerobic phototrophic Fe(II)-oxidizing bacterium *Rhodovulum iodosum*: implications for trace metal budgets in ancient oceans and banded iron formations

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It is widely accepted that anoxygenic photosynthetic bacteria (photoferrotrophs) oxidized dissolved Fe(II) in anoxic Archean seawater, leading to the sedimentation of Fe(III) minerals and cellular biomass, forming banded iron formations (BIF). However, it remains unknown to which extent the sedimented bacteria may have transported trace metals to BIF through their ability to sorb ions from seawater. We therefore chose the marine anoxygenic photoferrotroph Rhodovulum iodosum to quantify Cd²⁺, Co²⁺, Cu²⁺, Mn²⁺, Ni²⁺ and Zn²⁺ adsorption to bacteria/Fe(III)oxyhydroxide composites at neutral pH and an ionic strength of 0.1 M. Acid base titration data were modeled using a linear programming optimization method to yield pKa values of 4.83±0.13, 6.21±0.18, 7.74±0.24 and 9.28±0.27 and corresponding site densities of 5.7, 12.0, 3.3 and 6.5 x 10^{-4} moles/g, respectively. FTIR spectroscopy confirmed the presence of carboxyl groups as the most acidic sites corresponding to the lowest pKa values. The analysis of Cd²⁺ sorption data showed two metal complexing sites with pK_s values of 3.44 ± 0.14 and 4.80 ± 0.21 and corresponding binding site concentrations of $1.1\pm0.3 \times 10^{-4}$ and $0.9\pm0.2 \times 10^{-4}$ moles/g on the ferrihydrite/*R. iodosum* composite. The pKs values were used to calculate metal-ligand binding constants, Km. This confirmed Cd²⁺ binding to most acidic carboxyl groups on the ferrihydrite/R. iodosum composite surface, as the calculated Km was consistent with reported Cd²⁺ binding constants for simple organic acids (e.g., lactic, acetic, pyruvic and citric acid). This was used to further calculate the concentration of Co^{2+} , Cu^{2+} , Mn^{2+} , Ni^{2+} and Zn^{2+} sorbed to ferrihydrite/*R. iodosum* composites. The resulting concentrations were ultimately compared to the concentrations of trace elements in BIF to demonstrate that is plausible that the trace metal content in BIF was derived from plankton growing in the ancient ocean's photic zone.

The fate of biogenic vs. abiogenic organic matter during thermal maturation

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The discrimination of biogenic and abiogenic organic matter is still a central problem in geo- and astrobiology (e.g. [1, 2]). Indeed, alteration of these organic compounds over geological timescales makes an assignment of their origin problematic [3]. Experimental maturation studies provide the opportunity to observe molecular changes under controlled temperature and pressure regimes and could thus help in the interpretation of the underlying processes. Here we report on abiotic synthesis experiments to produce Fischer-Tropsch-type (FTT) organic material under hydrothermal conditions [4]. The FTT organics and a biogenic reference material (Green River Shale kerogen, Eocene) were experimentally maturated in gold capsules (e.g. 300°C, 1 d to 200 d, 2 kbars) to assess the molecular alterations and the stability of individual compounds during the maturation processes. We demonstrate that abiogenic FTT-processes can indeed produce a variety of linear-, branched-, and functionalized organic compounds that in many respects resemble biologically produced organic matter. Likewise, defunctionalisation and aromatisation reactions during maturation tend to make the molecular frameworks of biotic and abiotic organic matter essentially similar and thus, unspecific. It is therefore crucial to determine the distinct characteristics of biological organic matter that may remain even after strong alteration. The data obtained here contribute to a solid experimental fundament needed for the interpretation of organic signatures in Archean rocks and, potentially, extraterrestrial materials.

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Biogenic overgrowth on detrital pyrite in ~3.2 Ga old Archean paleosols (Moodies Group, BGB, South Africa). S. Nabhan et al.*

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Pyrite is a common mineral in the braided-fluvial sandstones of the lower Moodies Group of the BGB (~3.22 Ga). Regionally traceable paleosols within these strata contain locally abundant silicified nodules originally composed of pedogenic sulphates, interbedded with heavy-mineral laminae dominated by pyrite. A large proportion of this pyrite shows rounded detrital cores and secondary euhedral rims clearly different in their trace elemental compositions, then the cores. The cores show δ 34SVCDT values around 0‰ while overgrowth rims show values as light as -25‰. The negative δ 34SVCDT values, the close spatial association and the nearly contemporaneous formation of sulphate nodules and secondary pyrite rims is consistent with biogenic fractionation of sulphur in the paleosols. Microbial life was already present in the moist vadose zone of terrestrial environments about 3.2 Ga ago.

Ceres – a water-rich precursor to fill Earth's oceans

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As the only icy asteroid in the inner solar system, Ceres represents one of the key planetary building blocks. To fill Earth's oceans where life evolved, icy objects must have crashed into the planet, delivering water in the process. Isotopic evidence on 67P C-G indicates that water wasn't brought from large distances by comets. It was possibly delivered from the inner solar system by a class of bodies represented by Ceres. The major factors determining their water content are the accretion time, the initial dust to ice ratio and the orbit of the accretion. As a case study, we investigated the thermal evolution of a Ceres-like body and conditions sufficient for such objects to retain water by the means of a numerical model. The model includes accretion, reduction of the dust porosity, latent heat of ice melting, compaction driven water-rock separation, accretional heating, hydro-thermal circulation, solid-state convection of ice, and convection in a water ocean. We calculated differentiation models assuming an ice-rock composition based on the observations by Dawn. We investigated the implications for the availability of liquids and the possibility of cryovolcanism at present.

Triple oxygen isotope compositions of Archean ultramafic Rocks

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Earth likely accreted planetesimals that had variable mass-independent oxygen isotope compositions [1]. According to their W [2] and Pt [3] isotope compositions, some Archean rocks may have tapped a mantle source that had remained isolated from the last <2% of accreting materials. In search of a pre---late accretion signature in the oxygen isotope record, we analysed δ 180 and δ 170 in olivine from Archean ultramafic rocks from a variety of localities. Olivine from Cenozoic mantle xenoliths and basalts were analysed as reference for the post-Archean mantle. First results suggest that the triple oxygen isotope compositions of the Archean and post---Archean mantle were identical at the level of <4 ppm for Δ '170 and <0.15 ‰ for δ 180. If the Archean rocks in our sample suite indeed sampled a pre-late veneer mantle source, the presence of the following components during late accretion can therefore be excluded: >0.2% CO, CV, CM, CR chondrites, >0.4---0.6% ordinary chondrites, >1% CI chondrites. Measurements of W and/or Pt isotopes in these samples are required to test this interpretation. Interestingly, cumulate olivine from the ~3.0---2.8 Ga Ivnartivaq layered ultramafic complex in South---East Greenland [4] shows variable δ 180 values that are down to almost 3 ‰ lower than typical mantle olivine. We suggest that these low δ 180 values are primary and are best explained by the parental magmas having undergone assimilation of hydrothermally altered rocks. Based on combined δ 170 and δ 180 systematics, we show that the assimilated materials may have interacted with meteoric waters that had low $\delta 180$ values and were possibly of glacial origin. High-precision triple oxygen isotope measurements of the VSMOW2 international water standard relative to the San Carlos olivine rock standard are required to better constrain the oxygen isotope compositions of these Archean meteoric waters.

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Density and structure of amorphous silicate at high pressure conditions

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Modelling the formation and evolution of the deepest parts of the Earth through time requires the densities of solids and melts to be constrained. Other properties such as the structure and viscosity of high pressure melts are also needed to undersated the fate of deep mantle melts.

The main parameter controlling the entrainment or settlement of matter in the lowermost mantle and the possible deep magma ocean formation is the density contrast between solid and magma. To measure the density contrast between crystal and amorphous silicates, we have adapted the X-ray absorption method to the diamond anvil cell to enable density measurements of silicate glasses to be made to unprecedented conditions of high pressure [1]. We have consequently determined the densities of SiO₂ and MgSiO₃ glasses up to 90 and 127 GPa, respectively. We found that the glass and melts at CMB pressure can be as dense as their counterpart solids. Recently we extended the data to iron-bearing compsoition and we aim at forming a density model for amorphous silicate in the MgO-FeO-SiO₂ system. To understand the changes in the structure associated with such high densifictaion we measured the changes in the Si L-edge and O Kedge under pressure by means of X-ray Raman scattering as well as X-ray diffraction up to 70 GPa. For both method the data are of unprecedented quality and reveal details about the atomic structure of amorphous silicate at deep mantle pressure conditions. These new data will bring a deeper knowledge about the structural, polymerization and viscosity changes of silicate magmas at lower mantle pressures.

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Geodynamical implication of delamination on felsic crust generation during the Archean

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The geodynamic processes that were active during the Archean remain enigmatic. On the basis of geochemical and geological data, several working hypotheses exist, which suggest that the most crucial unsolved problems are: a) when and how was felsic crust generated and did this have geodynamic implications? b) how did cratonic lithosphere form and survive? c) did plate tectonics exist?

Here, we test the feasibility of some of these hypothesis with a c modelling approach, in which we couple chemical evolution and melt extraction using state-of-the art mafic thermodynamic mafi melting models with a viscoelastoplastic geodynamic finite element code. In our simulations, we test the effect of rheology of the mafic crust, melt weakening, the amount of intrusion, and the amount of melt extraction on the geodynamic deformation mode.

Our simulations show that under particular conditions, a plate like behavior occurs for a short amount of time, but also that the most stable mode of crustal recycling during the Archean is delamination of the eclogitic/restitic mafic crust. Delamination of the lower crust occurs rapidly and completely destroys the lithospheric mantle, putting the hot asthenosphere in direct contact with the mafic crust, which inducing a continuous generation of felsic crust. Continuous crustal delamination triggers significant mantle melting and thus mafic crust generation, and produces a cold crust similar to the recently proposed heat pipe model. This results in rapid mantle cooling, which suggest that the average cooling rate of the Earth has not been constant but rather fluctuated with time.

Our results show that under such kinds of conditions it is difficult to preserve lithospheric mantle, and that felsic crust production is rather rapid processes if mantle potential temperatures are sufficiently high.

A scaling law for melt volume produced by giant impacts

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During the late stages of planetary accretion, protoplanets experience a number of giant impacts and extensive mantle melting. The core of an impactor sinks through the molten part of the target's mantle (magma ocean) and participates in metal-silicate equilibrium where silicate and iron liquid react and exchange chemical elements. The iron sinks through the solid part of the mantle without further equilibration and it eventually merges with the core. Because element partitioning can depend strongly on the pressure and temperature conditions of equilibration, determining the impact-induced melt volume is a key for understanding the chemical evolution of planetary mantles and cores during early differentiation. Previous studies have developed scaling laws that describe melt volumes that are produced by small impacts, but we find that some of these laws overestimate giant impact-induced melt volume by orders of magnitude partly because they do not consider spherical geometry or self-gravity. In this study, we are developing a scaling law for melt volumes induced by giant impacts based on impact velocity, impact angle, impactor-to-total mass ratio, and the total mass, and is generally consistent with the melt volumes estimated with SPH calculations given that the standard deviation is less than 0.2 (the total mass considered here is 1-6 Mars masses). Our result has a number of implications for terrestrial planetary evolution, including predictions that the Moon-forming giant impact would have melted most of the Earth's mantle, while late accretion would not have caused significant melting of the Earth's mantle.

Evaporite pseudomorphs in the Paleoproterozoic Koegas Fm., South Africa

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Macroscopic textures in strongly silicified carbonate sediments of the Koegas Fm. resemble those in an evaporitic carbonate-sulfate tidal facies; the unit is overlain with erosional sharp contact by a glacigenic diamictite of ca. 2.425 Ga (Makganyene Fm). Raman data from Koegas samples document abundant calcite inclusions in large quartz crystals but yet fail to provide evidence of sulphates. CL images show laminations of probable microbial origin. The unusual facies contrasts between silicified evaporites overlain by the glacial tillite, the trace element patterns and the stable isotopes may be diagnostic of environmental conditions and may further constrain the interaction

between climatic drivers and sedimentary processes during the GOE.

Horizontal vs Vertical Tectonics in the Barberton Greenstone Belt

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The interior of the Barberton Greenstone Belt in South Africa consists of tightly and isoclinally folded, steeply plunging synclines. Despite being discussed since the early 60ies [1], the mechanism of their for-mation of this very distinctive folding pattern is still not understood. There are two contradictory mod-els: (1) cross folding (two single deformational events with contraction in directions perpendicular to each other); (2) Large-scale localized subsidence of dense greenstones into granitic crust and concom-itant plunge steepening towards the center of sub-sidence [2]. However, additional field data, such as cleavage patterns and a better understanding of the changes in plunge along the fold axes, is required in order to distinguish between these models.

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Implications of ¹⁴⁶Sm-¹⁴²Nd systematics on Paleoarchean volcanic and granitoid rocks from the eastern Kaapvaal Craton

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In this study we report the first high precision ¹⁴²Nd analyses for granitoids and amphibolites from the Ancient Gneiss Complex (AGC; Swaziland) and the Barberton Greenstone Belt (BGB; South Africa). The investigated samples span an age range of 3661 Ma to 3216 Ma representing the main geological units of the AGC and the lower Onverwacht Group of the BGB. Calculated μ^{142} Nd values range from -6.2 ± 3.1 ppm to +3.0 ± 3.0 ppm for most samples. Five samples show a tendency to slightly negative μ^{142} Nd anomalies that are, however, within error not unambiguously resolvable from the JNdi-1 standard (4.4 ppm 2 σ and 4.3 ppm 2 σ , respectively). The only confidently resolvable μ^{142} Nd anomalies are found in a 3442 Ma Ngwane Gneiss and the 3450 Dwalile Greenstone Remnant revealing μ^{142} Nd values of -7.9 ± 3.1 ppm (2se) and -6.2 ± 1.8 ppm (2 σ), respectively. Our results show that the inherited negative μ^{142} Nd anomalies in the eastern Kaapvaal Craton are the consequence of complex crustal reworking processes throughout the Paleoarchean. Such complex intracrustal differentiation processes have been previously proposed based on heterogeneous initial ϵ Hf values in zircons from the AGC

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New insights into the Paleoarchean meteorite bombardment of the Earth - Geochemistry and Re-Os isotope signatures of the BARB5 ICDP drill core from the Barberton Greenstone Belt, South Africa

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Archean spherule layers, resulting from impacts by large extraterrestrial objects, represent the only remnants of the early meteorite, asteroid, and comet bombardment of the Earth. Only few Archean impact debris layers have been documented, all of them embedded in the 3.23 to 3.47 billion year old successions of the Barberton Greenstone Belt (BGB) in South Africa and the Pilbara Craton in Western Australia. Some of them might be correlated with each other. Given the scarcity of Archean spherule deposits, four spherule layer intersections from the recently recovered BARB5 drill core from the central Barberton Greenstone Belt, analyzed in this study, provide a great opportunity to gain new insight into the early terrestrial impact bombardment. Evidence for minor to moderate hydrothermal activity indicates that element abundance signatures of spherule rich samples from the BARB5 drill core, at least in part, retained a meteoritic fingerprint. The impact hypothesis for the generation of the BARB5 spherule layers is supported by correlations between the abundances of moderately (Cr,Co,Ni) and highly siderophile (Re, Os, Ir, Pt, Ru and Pd) elements, whose peak concentrations and interelement ratios are within the range of those for chondrites. Rhenium-Osmium isotope evidence for a chondritic projectile further support the impact hypothesis. Collectively, this study provides evidence for extraterrestrial admixtures ranging between ~40 and up to 100% to three of the four analyzed BARB5 spherule layers, and a scenario for their genesis involving (i) impact of a chondritic bolide into a sedimentary target, (ii) varying admixtures of meteoritic components to target materials, (iii) spherule formation via condensation in an impact vapor plume, (iv) transportation of the spherules and sedimentation under submarine conditions, followed by (v) moderate post-impact remobilization of transition metals and highly siderophile elements.

Early mantle dynamics with non---linear rheology

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The rheology of planetary mantles is a function of temperature, pressure, strain rate, and grain size, whose relative importance strongly depends on the underlying deformation mechanism. The two most relevant are diffusion and dislocation creep. While the former depends on grain size, the latter shows a non-Newtonian behaviour due to a power-law dependence of the viscosity on the strain rate. The dynamics of the mantle is locally controlled by the mechanism that delivers the lowest viscosity. Yet the majority of global-scale convection models of the Earth and terrestrial planets are based on the use of a diffusion creep rheology with constant grain size. Here we used a mixed rheology to study the influence of various grain sizes on the dynamics of the mantle. The effects of non-Newtonian behaviour can be essential to understand the early dynamics of the Earth's interior, particularly with respect to the onset of convection and of different modes of surface tectonics following the solidification of the last magma ocean.

Geochemical modelling of triple oxygen isotope composition of seawater using high precision $\Delta'^{17}O$ analyses of terrestrial materials

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It has been long debated whether the $\delta^{18}O$ of seawater has remained constant at $0 \pm 2\%$ over geological time [1], or if it evolved from a very low value like -13‰ in the Archean to its present value [2]. The oxygen isotope composition of seawater is controlled by high- and low-temperature interactions with oceanic and continental crust. Here, we present a geochemical model of the triple oxygen isotope evolution of seawater over geologic time using high precision triple oxygen isotope analyses of altered oceanic crust samples and shale samples. High-T altered crust samples have $\delta^{18}O =$ $4.8 \pm 0.1\%$ and $\Delta^{17}O = -74 \pm 2$ ppm, whereas low-T altered basalts have $\delta^{18}O = 10.4 \pm 0.8\%$ and $\Delta^{17}O = 2 \pm 7$ ppm (relative to slope 0.5305).

The mass balance model yields modern seawater values within uncertainty, i.e., $\delta^{18}O = -1 \pm 0.5\%$ and $\Delta^{'17}O = -18 \pm 15$ ppm. We shall discuss the results with respect to oxygen isotope data of modern and ancient chemical sediments.

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High-precision W isotope measurements on Archean rocks from the Isua area, South-West Greenland Tusch*, J., Sprung*, P., Münker*, C., Hoffmann, J.E.

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Short-lived isotope systems are a useful tool for understanding processes that took place during the first tens to hundreds of million years of Earth's history. Of the short-lived systems, the ¹⁸²Hf - ¹⁸²W isotopic system (¹⁸²Hf \rightarrow ¹⁸²W + β^{-} , t_{1/2} = 8.9 Ma, [1]) has shown great potential to date geological processes back in the Hadean eon. Over the last five years, high precision W isotope measurement techniques by TIMS and MC-ICP-MS resolved ¹⁸²W heterogeneities in different terrestrial rocks, ranging in age from the early Archean to the Phanerozoic [2-7]. The finding of variabilities in ¹⁸²W in silicate rocks of different ages documents heterogeneities within the Earth's mantle that probably date back to Earth's early formation. In particular, several studies on rocks from the Isua area in the Itsaq Gneiss Complex (IGC) of southern West Greenland revealed resolvable excesses in ¹⁸²W for different lithologies [3,7].

Here, we report W concentration and high-precision isotope data, coupled with high precision high field strength element (HFSE) concentration and ¹⁷⁶Lu – ¹⁷⁶Hf isotope data for 3720 Ma boninite-like metabasalts from the Isua supracrustal belt (ISB) and 3400 Ma Ameralik dikes that later intruded into the ISB as well as a 2040 Ma Proterozoic Kangâmiut dike sample. Furthermore, our results were compared with published data including ¹⁴⁷Sm – ¹⁴³Nd, ¹⁴⁶Sm – ¹⁴²Nd and ¹⁸²Hf - ¹⁸²W isotope data for samples from the same lithological unit [3,8-9].

As results from our measurements, samples from the Ameralik dike suite show well resolved positive deviations for ε ¹⁸²W up to +0.15 as previously reported [3]. The boninite-like rocks also exhibit elevated ε ¹⁸²W values up to +0.20. Our study reveals positive initial ε Hf values for both rock suites from Isua that point to a derivation from an early depleted mantle source, which is also corroborated by ¹⁴⁷Sm – ¹⁴³Nd and ¹⁴⁶Sm – ¹⁴²Nd systematics from other studies. Thus, Hf/W fractionation during silicate melting within the early Earth's mantle during the lifetime of ¹⁸²Hf may have established high ¹⁸²W/¹⁸⁴W ratios in Isua. This conclusion is in accordance with interpretations by earlier studies [3,5]. However, a lack of correlation between W and Mg contents accompanied by an enrichment of W relative to elements with similar incompatibility in many samples (e.g. W/Th between 0.08 and 1.5) argue for a selective W mobilization by fluids, either during Archean subduction zone processes or during metamorphism. An inheritance of the radiogenic W isotope composition from metasomatic fluids can therefore not be ruled out. Tungsten fluid mobility in Archean rocks has previously been reported [4,6], but the mechanisms remained ambiguous which makes it challenging to assess the source and origin of the W isotope anomalies in Isua.

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The potential of coupled Hf-Nd isotopes to unravel geodynamical processes on Early Earth

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Coupled Hf-Nd isotopes in dissolved (< 0.2 μ m) and suspended fractions (> 0.2 μ m) of modern rivers and oceans are a powerful tool to understand weathering and erosion processes on the continents as well as the type and provenance of the weathered material [e.g., 1]. Here I present the potential of coupled Hf-Nd isotopes in Mesoarchean marine chemical sediments to (i) investigate the source(s) of elements in dissolved and suspended loads of marine environments on Early Earth and to (ii) unravel weathering and erosion processes that occurred on the earliest emerged continents. Neodymium isotopes reveal the impact of terrestrial and hydrothermal derived elements on ancient marine habitats. Since the extents and mineralogical

compositions of subaerial landmasses on Early Earth are incompletely understood, coupled Hf-Nd isotopes in contemporaneous marine chemical sediments will indirectly shed light on the mineralogical composition of the weathered continental landmasses. Furthermore, both isotope systems will help to evaluate if weathering and erosion of (ultra)mafic and/or evolved material were only local processes or were already a widespread phenomenon that had impact on the seawater chemistry of global oceans up to ~3.45 Ga ago.

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Volatile acquisition during terrestrial accretion: Solar wind (SW)-implanted Ne in cosmic dust

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Earth's present-day atmospheric noble gas inventory is assumed to have inherited its elemental and isotopic signatures from accreting planetesimals, mantle degassing, meteoritic additions and fractionation processes during Earth's early history [1-3]. The "planetary" composition of the atmosphere includes Ne isotopes with a 20Ne/22Ne ratio of 9.8, whereas the "solar" mantle composition rather resembles the solar wind implanted Ne-B in meteorites [4] (20Ne/22Ne ~12.5-12.7).

Considering protoplanetary disk lifetimes of a few to tens of millions of years [5,6], part of terrestrial accretion occurred after dissipation of the solar nebula [7]. This allows for implantation of high amounts of solar wind gases into objects with high surface/volume ratios in regions that are cleared from gas. Accretion of these objects to form proto-Earth might therefore supply sufficient solar gases to Earth's interior. Indeed, cosmic dust with large surface/volume ratios may have been of essential importance before the formation of Earth was terminated as the protoplanetary disk was still dust rich [8]. Implanted Ne-B has to be moreover considered as a significant source of the terrestrial noble gases as He and Ne in micrometeorites (MMs) and interplanetary dust particles (IDPs) are dominated by solar wind isotopic ratios [9] and MMs are currently dominating the extraterrestrial mass flux to Earth [10,11].

For our model approach we constrained the terrestrial influx for solid matter ranging from 10-16g–1025g. Furthermore, we compiled available Ne inventories of MMs and IDPs and complemented Ne data for other objects. The annual particle flux as well as the size and mass dependent Ne concentrations allow for calculation of the respective Ne flux to Earth. After setting a framework for the terrestrial accretion and scaling for early particle fluxes these values are used as basic input data to model the terrestrial Ne acquisition. We consider an early phase I of terrestrial accretion in a shielded disk environment, completion of accretion in a cleared disk, formation of a steam atmosphere and a magma ocean, degassing of accreted material and dissolution of solar gases into the magma ocean. The subsequent phase II occurs after atmospheric loss during the moon-forming impact, when mantle degassing and the late veneer completed the atmospheric inventory.

We performed model calculations fitting the current terrestrial atmospheric and mantle neon inventory and their isotopic compositions assuming a more moderately degassed plume-type mantle or a more strongly degassed MORB type mantle. The Ne isotopic composition of the late veneer has a strong influence on the mantle contribution to the atmosphere by mantle degassing, and hence, constrains also the terrestrial inventory of solar wind implanted neon during the early phase I. This inventory is limited by the depth of the magma ocean and the fraction of irradiated material. We find that low fractions of irradiated material are sufficient to explain the terrestrial neon inventory, even assuming a relatively shallow magma ocean.

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The carbon and nitrogen functional chemistry of organic matter in extraterrestrial samples.

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The provenance of the most pristine biomolecules, e.g., amino acids or nucleobases, on the early Earth is still a matter of debate [e.g., 1]. Starting from very simple CHON-bearing species such as CO2, H2CO, HCN, or NH3, complex polymerization reactions can either occur in the interstellar medium or the solar nebula, e.g., by irradiation of coated dust grains, on cometary or asteroidal parent bodies by aqueous alteration, or by reactions on Earth in the atmosphere or at mineral interfaces in hydrothermal systems. Disentangling these complex modification processes is important to understand the evolution of our current tableau of relevant biomolecules.

Extraterrestrial samples that have not suffered severe thermal overprint such as petrologic type 2-3 carbonaceous chondrites or interplanetary dust particles (IDPs) derived from asteroids and comets are suitable candidates to search for pristine biomolecules. These samples contain on average several wt. % of organic carbon mainly in the form of large kerogen-like molecules sometimes being isotopically anomalous in C, N or H.

The aim of this project is to locate organic matter in these samples "in-situ" by electron microscopy (SEM) and ion probe (NanoSIMS) techniques and to characterize the functional chemistry and mineralogy by low kV – UltraSTEM combined with high energy resolution – Electron Energy Loss Spectroscopy (EELS). This approach is less representative than bulk analyses on extracted organic matter performed since decades, but provides important information on unprocessed, single grains within their petrographic context.

Results on organic grains from CR chondrites (Renazzo, EET 92161) and IDPs confirm our previous findings that the polymerization of aromatic rings in the CR grains is increased, most likely due to subtle fluid-induced reactions on the CR parent body [2]. These polycyclic aromatic hydrocarbons are not directly relevant to early lifeforms, but could have served as scaffolds for the first primitive cell membranes. Other functional groups observed by EELS at the carbon K-edge include several types of C-O bonding environments (ketones, aldehydes,

carboxylic acids) that may act as precursors for a-amino acids via Strecker synthesis reactions [3] or for complex sugars via formose reactions [4]. Carbonate bonding is prevalent in all types of samples. Furthermore, we could document strong nitrogen functionality in the CR grains, but so far not in the IDP organics. This may indicate the importance of fluids for advancing polymerization and stabilization reactions of N-compounds or the presence of functionally different primary nitrogen reservoirs sampled by cometary and asteroidal samples. Nitrogen functionality is of particular importance, as for example C-N nitrile/imine and NH2- amine bonding environments are also precursors of amino acids, whereas N-heterocycles such as imidazole are important constituents of nucleobases. This is in accordance with recent observations by N-XANES on bulk samples [5].

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Continental crust formation: Abbreviated version

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At the beginning we discuss the geological background of our model. The focus of this paper is the temporal distribution of the generation of juvenile continental crust (CC). This CC-production is intrinsically tied to the thermoconvective evolution of the Earth's mantle. Therefore we numerically solved the full set of physical balance equations of convection in aspherical-shell mantle plus simplified equations of chemical CC-mantle differentiation. Our most significant conclusion is that the actual rate of CC-growth is NOT uniform through time. The kinetic energy of solid-state mantle creep, Ekin, slowly decreases with superposed early separated maxima, the temporal distribution of which is episodic but not periodic. The laterally averaged surface heat flow, qob, shows a similar behavior, but the qobpeaks have a time lag between 15 and 30 Ma compared to the Ekin-peaks. The CC-grow peaks have a delay of 75 to 100 Ma compared to the qob-maxima. The present-day qob- and CC-mass values are in good agreement with observation. Each CC-production episode is separated from the next one by a time interval of quiescence. The main cause for this result is not the variation of the mantle creep velocity but the fact that the peridotite solidus is not only a function of pressure but also of the water abundance. A differentiation period generates a regional water-concentration reduction and thereby an increase of the peridotite solidus and of the regional viscosity. By a plausible variation of parameters, we found a cluster of neighboring runs that reproduce the instants of time of the observed frequency peaks of zircon age determinations without essential change of the other results. Our calculated integrated CC-curve is situated near the curves of GLAM, Begg et al. (2009), Belousova et al. (2010), and Dhuime et al. (2012), however, our curve is not so smooth but shows distinct variations [1]. In order to guarantee reproducibility of our results but also for other geological applications, we publish the full sets of the Grüneisen parameter, peridotite solidus for three different water abundances, the viscosity profile factor, adiabatic temperature, thermal expansivity, and specific heat at constant pressure as a function of depth in Table B1.

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For numerical data (e.g., viscosity, Grüneisen parameters, mantle solidi, adiabatic temperature, thermal expansivity, and specific heat at constant pressure) see Appendix B. Supplementary sections and data of [1]. Further information can be found on http://www.geodyn.uni-jena.de

Phase equilibrium constraints on the formation and evolution of Earth's earliest continental crust

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Much of the Earth's oldest continental crust is composed of upper amphibolite to granulite facies "grey gneiss" which is dominated by metaigneous rocks of the tonalite-trondhjemite-granodiorite (TTG) suite. Most studies attribute the formation of these TTG protoliths to the partial melting of hydrated basalt at high pressures and temperatures. However, the exact pressures and temperatures involved are poorly constrained and hotly debated, and as a consequence so too are the possible tectonic conditions responsible for crustal formation. Existing models for melting conditions range from deep crustal conditions to pressures consistent with a subduction origin, based mainly on a combination of experimental and geochemical constraints. The recent development of a suite of thermodynamic models for minerals and melt for mafic to intermediate protoliths [1] has allowed the first robust calculations on such rocks, both in general [2] and for Archean continental crust [3-4]. These models allow us to calculate melt production, melt composition and the mineral assemblage of the residuum as a function of pressure, temperature and rock composition. Calculations on inferred mafic protoliths [5] show that deep crustal melting provides the most likely source region in terms of melt production composition and residuum, with much higher pressures associated with subduction unlikely to be viable due to significant subsolidus dehydration limiting melt production.

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Liquid and glass structure of Mg2SiO4 and MgSiO3 at high pressure

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For compositions of the Earth's mantle, the ratio MgO:SiO2 of approximately 1.3 lies between Mg2SiO4 forsterite and MgSiO3 enstatite. Therefore, physical and structural properties of melts with these compositions are of fundamental importance in understanding magma ocean processes in the young Earth, both at ambient and high pressure. While thermodynamic properties for Mg2SiO4 and MgSiO3 melts are very similar [1], their glass and melt structure at ambient pressure differ significantly [2,3]. This is most evident in the liquid structure factor SS(qq) at low wavenumber, representing long-range interactions. The first peak in SS(qq) for MgSiO3 lies at 2.0 Å-1, for Mg2SiO4 at 2.3 Å-1, with a significant satellite peak at lower qq [3,4]. Molecular dynamics simulations have predicted the satellite peak in Mg2SiO4 to disappear at high pressure in the melt for both the neutron and X-ray structure factor, due to cancelling contributions from the various partial structure factors [4]. However, shock wave experiments on Mg2SiO4 glass have observed it to be a persistent feature up to 100 GPa [5]. Here we explore by means of first-principles molecular dynamics simulations whether this satellite peak represents a memory effect from the ambient pressure glass structure or whether this a physical feature of the glass as it is compressed along the Hugoniot curve in shock wave experiments. We perform simulations at a few points on the Hugoniot, following two different strategies: (i) We follow the experiment by compressing the glass, initially equilibrated at ambient pressure and temperature; (ii) we cool to the target conditions from the molten state, first compressing the liquid and then cooling it to a glass. A comparison for results from these two distinct PP-TT paths will aid the interpretation of the experimental data.

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