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Building a Habitable Earth

Progress Report

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The following abstracts were prepared and collected for the planned General Meeting 2020 of the SPP 1833. Due to the restrictions imposed by the Covid-19 pandemic, it was not possible to hold this meeting. The present volume therefore represents a progress report of the research of the SPP 1833, as of March 2020.

All abstracts are given in alphabetical order of the first author.

Cadmium stable isotopes in the lunar regolith

Abouchami*, W., Wombacher, F., Braukmüller, N., Galer, S.J.G.
*Institut für Geologie und Mineralogie, Zülpicher Str. 49b, D-50674 Köln
wafa.abouchami@mpic.de

Mass-dependent stable isotope fractionation of volatile elements (Zn, K, Ga, Cd, Cl) in lunar rocks provide contrasting views on the origin, timing and processes that led to the formation of the Moon. The "giant impact" between the proto-Earth and Theia offers a generalized model for explaining the greater volatile element depletion of the Moon relative to the Earth, yet it remains unclear whether volatile loss occurred during a single, post-collision, large-scale evaporation event, during the lunar magma ocean phase or a combination of both phases [1 & references therein]. Here, cadmium isotopes provide important constraints on any evaporation/condensation processes. In addition, thermal neutron capture ^{113}Cd (n,γ) ^{114}Cd effects allow estimating the residence time of Cd in the upper few meters of the regolith which, in combination with Sm, Gd and/or Hf isotope data, yields some insights into the past cosmic-ray energy spectrum.

Here we present TIMS double spike Cd stable isotope measurements on six lunar samples, with an up to 20-fold improvement in analytical precision compared to previous data [1, 2, 3]. In order to distinguish between source (silicate-hosted) and process (vapor-transport) related Cd isotope signals in the regolith, leaching experiments were performed on Apollo 17 orange glass soil 74220 and Apollo 16 mature highlands soil 60500.

Our first results show large stable Cd isotope fractionation of up to ~5‰ amu^{-1}, substantially greater than those of terrestrial and carbonaceous chondrite samples measured alongside the lunar samples. Our data, along with those previously published [1, 2, 3] show that Cd stable isotopes, Cd abundances and *n*-capture effects correlate with the soil maturity index (Is/FeO). These trends suggest progressive Cd depletion of the lunar soils with loss of the lighter Cd isotopes during micrometeorite impacts and efficient impact gardening of the lunar regolith. By contrast, the Apollo 17 orange glass soil displays a distinctive light Cd isotope signature that is most likely acquired from the condensation onto glass bead surfaces of a Cd-rich vapor released during volcanic fire fountaining. This result is supported by the identical Cd isotopic signature of the orange glass leachate and that of the bulk, and its significantly greater enrichment in volatile elements compared to that of the highland soil leachate [4].

In summary, the observed correlations – when substantiated by additional data – potentially provide a means for reconstructing the "pristine" lunar regolith source composition and understanding the dynamics occurring at the lunar surface. Additional data, pending allocation of new samples, will be crucial for refining these first promising results regarding the origin and processes that defined the Moon's volatile and isotopic fingerprint.

[1] Day et al. (2020) EPSL 531, 115998

[2] Sands et al. (2001) EPSL 186, 103–111.

[3] Schediwy et al. (2006) EPSL 243, 326–335.

[4] Wombacher et al. (2008) GCA 72, 646–667.

[5] Wombacher et al. (2020), see this report p. 25

The first self-consistent modeling of collisional water transport during late-stage planet formation by an Nbody – SPH hybrid code

Burger*, C., Schäfer, C. M., Bazsó, Á., Maindl, T. I.
*Institute of Astronomy and Astrophysics, University of Tübingen, Germany
christoph.burger@uni-tuebingen.de

The final phase of terrestrial planet formation, where protoplanets and remaining planetesimals accrete into planets, is a dynamically stochastic process, marked by giant collisions and radial mixing of material over wide orbital distances. Several approaches for treating collisions beyond (over-)simplified perfect inelastic merging have been developed in recent years, but none has been designed nor applied to model the evolution and delivery of water and other volatiles, even though particularly susceptible to collisional transfer and erosion. To close this gap, we have developed a hybrid framework to directly combine long-term N-body integrations with dedicated Smooth Particle Hydrodynamics (SPH) simulations of all individual collisions. This allows us to self-consistently model the compositional evolution on a system-wide scale for the first time [1], including frequent hit-and-run events, where not only material/water losses but also transfer between the colliding bodies is decisive. We apply our framework to terrestrial planet formation in a solar-system-like setting, and find that with a realistic collision treatment final water contents are reduced towards more Earth-like values by a factor of two or more. In addition, accretion timescales are significantly lengthened (to 100-200 Myr and more) when fragmentation and hit-and-run events are realistically modeled. Our results show that water delivery is dominated by very few decisive collisions (accretionary and frequently also hit-and-run), with Moon-to-Marssized or even larger impactors. Even though our model includes their collisional evolution, smaller bodies seem to play only a minor (direct) role in water transport to potentially habitable planets. Beyond this first application, we believe that this methodology offers a solid basis for including further decisive physical processes, towards a deeper understanding of terrestrial planet formation and evolution.

[1] Burger, C. et al. (2020) Astronomy & Astrophysics 634, A76.

A novel magma ocean-atmosphere model to provide input for the early Archean Earth composition

Carone*, L., Barth, P., Barnes, R., Noack, L. Molliere, P., Driscott, P.
*MPIA, Königstuhl 17- 69117 Heidelberg, Germany
carone@mpia.de

We present here the novel magmal ocean model MagMOC[1] and first results applied to Earth. We included energy-limited and diffusion-limited atmospheric escape of water and oxygen [2], equilibrium tides [3], and the radiogenic heating from 26Al, 40K, 232Th, 235U, and 238 U.

With this model we simulate the early evolution of Earth, assumiming silicate Earth, a 1;5 ratio between outgassed water vapour and carbon-dioxide and initial volatile content of 2- 20 terrestrial oceans. We compare our results to previous models by [4] and [5]. We find that we generally reproduce their results, however, we built up twice as much water than Elkins for the wet scenario (20 terrestrial ocean) and in our model CO2 remains initially completely solved in the magma during the dry scenario (2 terrestrial ocean). We agree better with [5], but solidify the magma ocean earlier (2 Myrs compared to 4 Myrs). Our magma ocean model will be adapted in the future to also tackle a reduced mantle composition and the influence of the Moon impactor. The magma ocean and the atmosphere composition derived by this model will provide valuable input for the early Archaean Earth scenario, in particular on the water and CO2 content.

[1] Barnes, R., Deitrick, R., Luger, R., et al. 2018, Vplanet: Virtual planet simulator, Astrophysics Source Code Library
[2] Watson, A., Donahue, T., & Walker, J. 1981, Icarus, 48,150
[3] Ferraz-Mello, S., Rodriguez, A., & Hussmann, H. 2008,Celestial Mechanics and Dynamical Astronomy, 101,
[4] Elkins-Tanton, L. T. 2008, Earth and Planetary Science Letters,271, 181
[5] Hamano, K., Abe, Y., & Genda, H. 2013, Nature, 497, 607

Is nitrogen fixation by *Nostoc sp.* PCC7524 increased in a simulated early earth atmosphere?

Katharina Ebel*, Thorsten Bauersachs, Achim Herrmann and Michelle M. Gehringer
*Department of Microbiology, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany
kebel@rhrk.uni-kl.de

The filamentous cyanobacterium, *Nostoc sp.* PCC7524, produces specialised cells known as heterocytes, which house the oxygen sensitive nitrogenase responsible for biological nitrogen fixation (BNF). The thick heterocyte cell wall reduces oxygen diffusion and contains specific glycolipids that are used as biomarkers for heterocystous cyanobacteria and BNF. Despite evidence of oxygen rich niches during the mid-Archean eon, there was no free oxygen in the Earth's atmosphere until the Great Oxidation Event (GOE), ~2.4 Ga. The delay in the expansion of early oxygenic phototrophs is thought to have been restricted by the availability of biologically accessible N. The aim of this project is to determine the effects of an oxygen free atmosphere and elevated CO_2 levels on BNF, photosynthesis and heterocyte glycolipid ratios. As climate change leads to elevated CO_2 in the present atmosphere, the understanding of the past may allow the prediction of changes in BNF, photosynthesis and glycolipid contents in heterocystous cyanobacteria in the future.

Nostoc sp. PCC7524 was acclimatised to three different atmospheres under identical growth conditions: present atmospheric levels of O_2 and CO_2 (PAL), elevated CO_2 conditions (eCO_2) at 2000 ppm and an Archean atmosphere without O_2 at 2000 ppm CO_2. Differences in expression of the nitrogenase *nifD* and Rubisco *rbcL1* genes were measured *via* qRT-PCR and compared to protein levels using western blotting. N-fixation and oxygenic photosynthesis rates (O_2 generation) were also determined. Additionally, the heterocyte glycolipid, glycogen and protein content of end point cultures were measured.

Our results did not show any significant changes in growth rates for either diazotrophic nor non-diazotrophic conditions under Archean or eCO_2 atmospheres. However, the glycogen and protein content of the Archean endpoint cultures were substantially raised when compared to those grown under PAL conditions. For cultures grown diazotrophically under an eCO_2 atmosphere, the glycogen and protein contents were not increased. N-fixation was probably the limiting factor due to oxygen stress impairing the further accumulation of C- and N-storage compounds. However, under non-diazotrophic growth conditions in the climate change scenario glycogen and protein contents were higher compared to PAL, as carbon fixation was enhanced by eCO_2 and was not N limited. Heterocyte glycolipids were present in the differently grown cultures, supporting their use as biomarkers of BNF. Data generated in this study will offer greater insight into BNF in heterocystous cyanobacteria under future (eCO_2) and past (Archean) atmospheric conditions. Additionally, our study provides a novel view into the delay in the expansion of early cyanobacteria prior to the GOE.

Investigation into Fe^{2+} Toxicity in Cyanobacteria grown in a Simulated Archean Ocean

Enzingmüller-Bleyl, TC. Herrmann, A. Gehringer, M.
Department of Microbiology: Technische Universität Kaiserslautern, Kaiserslautern, Germany
bleyl@rhrk.uni-kl.de

The availability of iron, particularly in modern oceans, affects the growth of living organisms. Cyanobacteria, essential primary producers in both terrestrial and marine environments, require iron to build and maintain their photosynthetic machinery. Prior to the Great Oxygenation Event (GOE), iron was abundantly available as soluble Fe^{2+} in the Archean ocean, with concentrations ranging from 40 to 120 µM. Fe^{2+} concentrations of 120 µM were demonstrated to be toxic to modern day marine cyanobacteria (E. D. Swanner *et al*., 2016). Proto-cyanobacteria needed to adapt to high Fe^{2+} concentrations to survive and presumably cause the GOE. Research on modern day cyanobacteria have identified numerous receptors associated with the uptake of Fe^{2+}/Fe^{3+}.
Our aims are: To determine the distribution of core iron uptake genes among modern and basal lineages of cyanobacteria and to specifically investigate iron uptake receptors and the potential toxicity of Fe^{2+} in the marine oxygenic phototroph *Pseudanabaena* PCC 7367. Additionally, we compare the role of FeoB, a dedicated Fe^{2+} receptor, on iron toxicity in the freshwater strains, *Microcystis aeruginosa* PCC7806 and 9432.
Essential iron uptake transporters and regulators were identified using *in silico* analysis. The *feoB* gene was mostly absent in basal clade cyanobacteria with *Thermosynechococcus elongatus* BP-1, *Acaryochloris sp.* CCMEE 5410 and *Cyanothece sp.* PCC 7425 the only exceptions. Alignments were constructed in MUSCLE (MUltiple Sequence Comparison by Log-Expectation) and used to generate gene phylogenies using MEGA (maximum likelihood, 1000 bootstraps). Primers for quantitative RT-PCR targeted the following iron uptake genes: *fur* (iron homeostasis), cFTR1 (iron permease), ARTO (iron reduction) and *rpoC1* (reference gene). Expression of these genes were determined in late exponential phase cultures of *Pseudanabaena* PCC 7367, in medium containing 120 µM Fe^{2+} over 24 hours, under an Archean-like atmosphere while levels of Fe^{2+} were monitored. The potential role of FeoB on iron toxicity in cyanobacteria was determined by growing strains with (*Microcystis aeruginosa* PCC 7806 and 9432) or without the *feoB* gene (*Pseudanabaena* PCC 7367 and *Synechococcus* PCC 7336) in 120 µM, 240 µM and 360 µM Fe^{2+} under Archean conditions.
Pseudanabaena PCC 7367 could grow and survive in a simulated Archean atmosphere (A. Herrmann, personal communication, Dec 27, 2019). Expression levels of ARTO changed in relation to available Fe^{3+}, while a gene encoding the iron uptake transporter cFTR1 reduced expression after Fe^{2+} addition. Our data challenges the paradigm that Fe^{2+} was toxic to early ocean growing cyanobacteria, possibly because they lacked the Fe^{2+} uptake gene *feoB*.
The data generated in this study provides greater insights into the evolution and diversity of cyanobacterial iron uptake mechanisms in the lead up to the GOE as well as the potential role of FeoB in Fe^{2+} toxicity.

Ga/Al ratios in ferromanganese nodules and crusts and the development of a potential proxy for Precambrian BIF

Ernst*, D. M., Schier, K., Garbe-Schönberg, D., Bau, M.
*Jacobs University Bremen, Campus Ring 1 – 28757 Bremen - Germany
d.ernst@jacobs-university.de

The origin of the prominent banding in banded iron formations (BIF) is still controversially discussed, with some suggesting a primary depositional and others a secondary diagenetic origin. The development of Ga/Al ratios as a new source proxy for early Precambrian BIF may allow to verify the reliability of the Ge/Si source proxy that provides new insights into element fluxes into early Precambrian oceans. Gallium and Aluminium are geochemical partners, similar to Ge and Si, and show coherent geochemical behaviour in igneous and clastic rocks. However, they are fractionated during weathering and hydrothermal water-rock interaction, resulting in Ga/Al ratios in modern seawater that differ from those of high-temperature hydrothermal fluids and continental runoff. A prerequisite for the succesfull application of such a new geochemical proxy, however, is the verification of the robustness of potential geoarchives that host this proxy. As a first step we investigated hydrogenetic marine ferromanganese nodules and crusts to see whether the Ga/Al ratios of these oxidic precipitates reflect the ratio of ambient seawater. The determination of Ga and Al concentrations in ferromanganese crusts and nodules was done by the complementary in-situ High-Resolution Laser-Ablation ICP-MS analyses of polished sections and nano-pellets [1] and of dissolved samples. Preliminary results suggest that Ga/Al ratios of ferromangenese crusts and nodules are lower than those of seawater suggesting preferential scavenging of Al over Ga.

[1] Garbe-Schönberg, D., Müller, S. (2014) J. Anal. At. Spectrom. 29, 990 – 1000.

A single UHT metamorphic event from 2.7 Ga to 2.5 Ga in the central region of the Lewisian Complex, Scotland

Gutieva, L.*, Dziggel, A., Johnson, T.E.
*Institut für GMG, Ruhr-Universität Bochum, Universitätsstraße 150, 44801, Bochum, Germany
Lanita.Gutieva@rub.de

The Lewisian Gneiss Complex (LGC) in NW Scotland, a classic example of Archean lower crust, is traditionally divided into three regions separated by crustal-scale shear zones and exhibiting different metamorphic facies. A smear of concordant U-Pb zircon ages between c. 3.0 and 2.5 Ga [1] from the granulite-facies central region has been interpreted as metamorphic resetting of earlier magmatic and metamorphic ages during two discrete high-temperature metamorphic events at 2.7 Ga and 2.5 Ga, “Badcallian” and “Inverian”, respectively [2]. More recently, this spread was re-interpreted to reflect the continuous recrystallization of zircon at suprasolidus conditions during a single tectonothermal episode [3]. Our structural and petrological investigations are consistent with the single high-temperature metamorphic event in the central region that lasted for >200 m.y. The granulite facies assemblages are best preserved in mafic rocks, while the TTG gneisses contain only relict granulite facies mineralogy, most evident away from the shear zones. At these locations a shallow- to moderate W- to NW-dipping “Badcallian” fabric in TTG gneisses is mainly defined by later retrograde amphibolite facies assemblages. This amphibolite facies overprint becomes dominant approaching large steep shear zones characterized by SW-dipping “Inverian” and late Paleoproterozoic (“Laxfordian”) subvertical fabrics. The Inverian and Laxfordian foliations are also predominant throughout the gneisses of the southern and northern regions, where we found no evidence of granulite facies metamorphism or Badcallian structures. Our field observations suggest that the Badcallian structures initially formed when the central region was melt-bearing, but these structures were progressively overprinted during slow syn-kinematic cooling to amphibolite facies, likely at 2.5 Ga. This is supported by the recent zircon geochronological data from a 2.6 Ga monzogranite sheet [3] that further questions the idea of two distinct metamorphic episodes.

[1] Goodenough, K.M. et al. (2013) Precambrian Research 233, 1–19.

[2] Corfu, F. et al. (1994) Contributions to Mineralogy and Petrology, 117, 215–228.

[3] Taylor, R.J.M. et al. (2020) Geology 48, XXX–XXX.

Temporal evolution of the atmosphere and oceans across the Great Oxidation Event

Julius C. Havsteen[1], Gareth Izon[2], Nicolas J. Beukes[3], Bradley Guy[3], Harald Strauß[4], Lucile Roué[1], Benjamin Eickmann[1], Ronny Schoenberg[1, 3]
[1]Eberhard Karls University Tübingen, Institute for Isotope Geochemistry, Tübingen, Germany
[2]Massachusetts Institute of Technology, Department of Earth, Atmospheric and Planetary Sciences, Cambridge, USA
[3]University of Johannesburg, Department of Geology, Johannesburg, South Africa
[4]University of Münster, Institute for Geology and Paleontology, Münster, Germany
Julius.havsteen@uni-tuebingen.de

It is now generally accepted that a major requirement to make the Earth a habitable planet, with biological evolution from single-celled organisms to higher life forms, is the accumulation of free oxygen in the atmosphere-ocean system. The Earth has undergone several pulses of progressive atmospheric oxygenation towards the present level of 21 % molecular oxygen (which translates to 100 % for the present atmospheric level (PAL) of oxygen). Here we present redox sensitive major -and trace element systematics and multiple sulfur isotope data from the earliest stage of Earth's oxygenation history across the ~2.45 to 2.32 Ga Great Oxidation Event (GOE). Among several indicators in the rock record for increased atmospheric O_2 levels at this time, the most pronounced is the disappearance of mass independent fractionation of sulfur isotopes (MIF-S), which only occurs photochemically at atmospheric O_2 concentrations of less than 0.001 % PAL.

Far more controversial is whether the GOE happened as a sharp, single step or as an oscillating, multistage event. Guo et al. (2009) identified a sharp disappearance of MIF-S signatures in the rock record of the Transvaal sub-Basin, South Africa. However, improved age dates for the Ongeluk Lava in the adjacent Griqualand West sub-Basin reported by Gumsley et al. (2018) significantly changed the stratigraphic correlation between the Transvaal and Griqualand West sub-Basins and opened the possibility for fluctuating oxygen levels across the GOE.

In this study we try to shed light on this matter by using redox tracers to carefully map the chemostratigraphic evolution of relevant strata in the Transvaal sub-Basins. Access to drill cores from the Agouron GOE and Biomarker Drilling Project, enables us to compare geochemical data over different depositional settings and helps us to better constrain stratigraphic discrepancies.

Geochemical redox signals of the AGP-1 drill core appear to be muted compared to similar studies of MIF-S signals (Guo et al., 2009; Luo et al., 2016) and redox-sensitive element systematics (Anbar et al., 2007), which makes clear interpretations about the redox evolution during ongoing sedimentation in this core difficult. Pyrite petrography and morphology in the AGP-1 core reveals recrystallization, most likely due to metasomatic activity related to the intrusion of the Bushveld Igneous Complex, which may explain the relatively muted redox signals and $\Delta^{33}S$ signal. However, our preliminary results show a clear shift from MIF-S to mass dependent isotopic fractionation of sulfur (MDF-S) in the lower part of the upper Duitschland/Rooihoogte Formation. The shift from MIF-S to MDF-S goes along with a continuous decrease in $\delta^{34}S$ values from +1 to -23 ‰ as a result of increasing levels of biogenic sulfate reduction. This observation may imply enhanced continental oxidative weathering and the build-up of a significant oceanic sulfate pool and thus provides multiple evidence for a significant increase of atmospheric and oceanic oxygen levels at this stratigraphic position.

Trace element concentrations of Mo and U are generally low throughout the entire core, with small covariations observable especially in the upper part of the core. Future $\delta^{98/95}Mo$ and $\delta^{82/76}Se$ data may help to constrain the role of various Mo and Se sources to the sediments and to identify the redox state of the water masses.

Surviving the ferruginous Archean ocean – Assessing the potential toxicity of Fe(II) on basal Cyanobacteria under anaerobic conditions

Herrmann, J. A. and Gehringer, M. M.*
*Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 1, D-67663 Kaiserslautern, Germany
mmgehringer@yahoo.com

The oxygenation of early Earth's atmosphere ~2.4 Ga ago, known as the Great Oxygenation Event (GOE) was presumably caused by oxygenic photosynthesis by Cyanobacteria. The Archean atmosphere is thought to have contained 0,2-1% CO_2 while the oceans were anoxic with high levels of Fe(II) (40-120 µM Fe(II)). Recent studies suggest that Fe(II) concentrations of >100 µM are toxic to modern, marine Cyanobacteria, thereby modulating their expansion in the ferruginous Archean oceans. These studies utilised closed culture systems with highly elevated CO_2 levels of 10%. This study investigated the potential toxicity of Fe(II) on two basal strains of cyanobacteria in an atmosphere representing the Archean, in both a closed (10% CO_2) and open culture system at 0.2% CO_2.

Pseudanabaena PCC7367 and *Synechococcus* PCC7336*,* were incubated under an anoxic, elevated CO_2 atmosphere in buffered ASNIII media with increasing Fe(II) concentrations (15 µM, 120 µM & 600 µM). Chl a determinations were used to track cell growth over 21 days, while the ferrozine assay reported the oxidation of Fe(II) to Fe(III). The O_2 levels in the closed system were logged in order to record the build-up of O_2 and calculate its production rates. Additionally, liquid cultures were subjected to repeated nightly additions of 120 µm Fe(II) to simulate a tidal inflow of ferruginous Archean ocean water at night.

While the closed system cultures indicated a similar Fe(II) toxicity response to that seen in the literature, the cultures grown in an open system showed increased growth with significant increases in glycogen and protein content. A significant build-up of oxygen was observed in the closed culture bottles, suggesting a basis for the observed reduced growth. The cultures exposed to a daily influx of Fe(II) showed that basal cyanobacteria can tolerate concentrations of Fe(II) in the range found in Archean oceans during the night time. Additionally, we can report the precipitation of green rust under certain experimental conditions, which had a strong inhibitory effect on cyanobacterial growth.

Overall our results suggest that, in an open culture system, iron would not have been toxic to *Pseudanabaena* PCC7367, while it reduced the growth rate of *Synechococcus* PCC7336 at 120 uM Fe(II)/ Fe(III). Future work will focus on the influence of Fe(II) on cyanobacterial pseudo mats and the localisation of iron oxidation in a tidal system.

Quartzofeldspathic Moodies sandstones (Barberton Greenstone Belt, BGB, ~3.22 Ga) are derived from intra-GB felsic igneous rocks, not from extra-GB granites

Heubeck, Christoph*; Janse van Rensburg, Deon*; Reimann, Sebastian*
*Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, 07749 Jena, Germany
christoph.heubeck@uni-jena.de

"Cratonization" is a contentious term which may, among other characteristics, include the first-time access of granite to surface systems across large subaerial (i.e., continental) surfaces. The thick quartz- and feldspar-rich terrestrial and shallow-water sandstones of the Moodies Group of the Barberton Greenstone Belt, South Africa and Eswatini, have at times been considered to represent such a signal, a view also at times held by the first author, thus constraining the age of the Kaapvaal craton. Several lines of evidence, however, suggest an orogenic, intra-greenstone belt origin for these voluminous sandstones rather than an enigmatic, now completely eroded extra-GB granitic source: (1) Texturally and mineralogically supermature Moodies sandstones can be traced updip into highly immature, feldspar-porphyry-rich conglomeratic debris flows and matrix-rich sandstones rimming the Onverwacht Anticline, the suspected source area, consistent with paleocurrents; (2) The up to 2.5 km thick rhyodacitic and coarse-grained volcaniclastic unit H6 of the Onverwacht Anticline, representing a stage of felsic volcanism in the upper Onverwacht Group at ~3445 ± 4 Ma, and some units of the Schoongezicht Fm. (ca. 3227 Ma) show abundant microcline and monocrystalline quartz, morphologically identical to grains in Moodies sandstones; (3) detrital zircon age spectra of Moodies sandstones suggest dominant contributions from felsic igneous rocks of both ages and generally lack indications of extra-GB sources; and (4) Moodies conglomerates sampled in proximity to the suspected source area are in places dominated by feldspar porphyry clasts, some of which are packed with phenocrystic megaquartz, resembling granite. This clast type, however, is subject to rapid mechanical breakdown and therefore quickly eliminated from the Moodies clast spectrum with increasing transport distance. The quartz- and feldspar-rich character of Moodies sandstones does therefore not reflect crustal stabilization of the Kaapvaal craton by buoyant, high-level, now eroded felsic plutons.

The rapidity of textural (sorting, rounding, clay removal) and mineralogical (Q-, F-content) maturation with increasing distance from the source area within a few km may allow the modelling and constraining of Archean weathering conditions. Preliminary data indicate a high atmospheric P_{CO2}, possibly aided by strong tidal action, episodic and increased rainfall, and higher temperatures.

Evidence for PGE-enriched domains in the mantle sources of 3.46 Ga meta-komatiites from Dwalile Greenstone Remnant, Swaziland

Hoffmann, J.E.*, Gans, P.
Institut für Geologische Wissenschaften, Freie Universität Berlin, Germany, Malteserstr. 74-100, D-12249 Berlin
*jeh@zedat.fu-berlin.de

Increasing PGE abundances in the sources of komatiites have been interpreted to reflect protracted mixing and homogenization of late accreted material into the Earth's mantle throughout the Archean [1]. In contrast, Eoarchean peridotites from southern West Greenland show already almost the full inventory of the PGEs [2].

Here we report PGE abundances and Re-Os isotope systematics of well-characterized serpentinized komatiites from the 3.46 Ga Dwalile Greenstone remnant, eastern Kaapvaal craton (Swaziland) to place constraints the PGE contents of their mantle sources. Interestingly, the PGE patterns are diverse and different to the Barberton and Schapenburg komatiites. Depletion of PPGE and Re indicate a depleted mantle source. Five of ten samples yield PGE abundandes exceeding the primitive upper mantle estimate [3]. The best preserved samples yield initial 187Os/186Os isotope compositions as low as 0.1034 at 3.46 Ga. These samples lie on an age regression line of 3543 ±140 Ma (n=5; MSWD = 2.3) indicating the preservation of Re-Os systematics.

Our findings indicate, that reservoirs existed within the Paleoarchean mantle that had higher abundances of PGE than the average modern mantle. Yet, only lower abundances have been reported based on komatiite analyses [e.g., 4]. This suggest strong heterogeneities for the PGE in the Archean mantle that may suggest incomplete mixing of late accreted material.

[1] Maier, W. et al. (1968) Nature 460(7255), 620-623.

[2] van de Löcht, J. et al. (2018) Geology 46(3), 199-202.

[3] Becker et al. (2006) GCA 70, 4528-4550.

[3] Puchtel, I.S. et al. (2016) Geochem. Geophys. Geosyst. 17(6), 2168-2193.

Tracing the rise of continents using the triple oxygen isotope composition of carbonates?

Oliver Jäger*, Jakub Surma, Nina Albrecht, Chris S. Marien, Wanli Xiang, Katharina Schier, Michael Bau, Joachim Reitner, Andreas Pack
*Geowissenschaftliches Zentrum Göttingen, Goldschmidtstraße 1, D-37077 Göttingen, Germany
oliver.jaeger@uni-goettingen.de

Oxygen isotopes are a widely used tracer in the field of palaeoceanography and provide unique information on mineral formation and environmental conditions. The oxygen isotope record of marine chemical sediments displays a continuously rise in $\delta^{18}O$ of 10 to 15‰ from the Archean towards the Phanerozoic. Three scenarios are suggested to account for this isotopic shift: (I) a decline in the ocean surface temperature from the Archean to the Phanerozoic, (II) an Archean ocean, that is depleted in ^{18}O compared to present day and (III) modification of the primary isotopic composition due to alteration by meteoric water [1]. Here we present first high-precision triple oxygen isotope data of Precambrian carbonates and an alternative explanation for the observed secular trend in $\delta^{18}O$ and $\Delta'^{17}O$ of chemical sediments. The data show that Precambrian carbonates were not in equilibrium with seawater with a composition similar than today. Instead, we suggest that the data are explained by oceans with a few ‰ higher $\delta^{18}O$ and lower $\Delta'^{17}O$. The change in ocean isotope composition can be explained by a lower rate of continental weathering [2]. This would point to a smaller continental surface ("water world") and/or lower weathering rates.

[1] Shields and Veizer, 2002, G^3, 10.1029/2001GC000266

[2] Sengupta and Pack, 2018, 10.1016/j.chemgeo.2018.07.012

Interaction of (sub-)volcanism with shallow-water sedimentary dynamics: News from the Paleoarchean Moodies Group (3.22 Ga), Barberton Greenstone Belt

Janse van Rensburg*, D. J., Reimann, S., Heubeck C.
*Institut für Geowissenschaften, Friedrich-Schiller Universität Jena, Burgweg 11, 07749 Jena, Germany
dj.j.van.rensburg@uni-jena.de

The up to 3.7 km thick Moodies Group has classically been described as a synorogenic sequence of quartz-rich sandstone, conglomerate, and fine-grained sediments with subordinate ferruginous sediments and volcanic components. A basaltic lava (MdL) approx. mid-section is the best marker unit and marks BGB-wide changes in facies trends, tectonic regime, and sandstone petrographic composition [1]. This unit is but one part of the larger Moodies igneous complex (MIC) which, aside from the aforementioned basaltic lava and associated tuffs, also consists of plutonic sills (the large Lomati River Intrusive (LRI) and the smaller Sterkspruit Sill), and an extensive subvolcanic stockwork complex. This (sub-)volcanic component to the Moodies Group and its interaction with the surface has not been studied in detail. MdL thickens considerably to the east into the Eswatini part of the BGB where it appears to form a shoreline basaltic flow complex. The subvolcanic stockwork, of which some dikes may have acted as feeders to MdL, is pronounced in the central BGB, and includes at least one diatreme. Numerous spectacular outcrops show features indicative of rising basaltic magma and lava interacting with water-rich unconsolidated sandy sediment.
In the central BGB, Moodies strata are extensively bleached, recrystallized, fractured, altered or mineralized by hydrothermalism and metasomatism in the km-wide aureole of the MIC. Silica-rich hot water may have erupted as fumaroles, geysers, and/or hot springs and cooled in widespread fluvial, deltaic and tidal environments
We will use geochemical (whole-rock geochemistry, microprobe analysis, petrography) and geological tools (detailed mapping and outcrop documentation, cross section balancing, age dating) to resolve the complex near-contemporaneous temporal and close spatial association of magmatism, sedimentation, deformation, and hydrothermal alteration in the Moodies Group. This, in turn, will test whether the wordwide unique excellent preservation of abundant tidal- and fluvial-facies microbial mats in the regional halo of the sills (and only there!) is due to early silicification. Our findings will also allow a more quantitative reconstruction and understanding of the permobile character of this exemplary Paleoarchean greenstone belt.

[1] Heubeck, C., 2019, The Moodies Group - A high-resolution archive of Archaean surface and basin-forming processes; in: A. Kröner and A. Hofmann (eds.), The Archaean Geology of the Kaapvaal Craton, Southern Africa. Springer (Regional Geology Reviews), p. 203-241.

The continued quest to find the signs of in situ ^{60}Fe decay in primitive meteorites

Kodolányi*, J., Hoppe, P., Vollmer C., Berndt, J.
*Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, D-55128 Mainz, Germany
j.kodolanyi@mpic.de

The role of ^{60}Fe (t½ ~ 2.60 × 10^6 years) as a heat source for the differentiation of early Solar System bodies depends on its initial Solar System abundance. However, initial $^{60}Fe/^{56}Fe$ ratios inferred from bulk rock and in situ mineral data differ by up to two orders of magnitude (with in situ data suggesting a higher initial ratio; e.g., [1,2]). This puzzling discrepancy poses the question: Was there any time or place in the early Solar System, when/where ^{60}Fe was present at a significantly higher level, than the level suggested by bulk meteorite data ($^{60}Fe/^{56}Fe$ ~1 × 10^{-8}, [2])? In order to give an answer, we have been trying to find evidence for the in situ decay of ^{60}Fe in primitive carbonaceous and ordinary chondrites, using the NanoSIMS. We measured troilite and olivine so far, without any constraints on their age. Although at the spatial resolution of our measurements (2–3 µm) alteration products or metal inclusions are readily avoided, we found no evidence for the in situ decay of ^{60}Fe. In fact, we found no significant $^{60}Ni/^{62}Ni$ anomalies relative to solar at all, even though we analysed phases with higher $^{56}Fe/^{58}Ni$ ratios (~500,000) than those measured in previous studies that reported data supporting in situ ^{60}Fe decay (maximum $^{56}Fe/^{58}Ni$ ratio ~50,000; [1]). Focussed ion beam slices of two analysed troilite grains have been investigated using transmission electron microscopy (TEM). The TEM data do not prove or refute unequivocally that the troilites gained or lost nickel after their formation. We are currently trying to find as old chondrules as possible (using initial $^{26}Al/^{27}Al$ ratios inferred from NanoSIMS data), with iron-rich, but nickel-poor phases, where the chance of finding evidence for in situ ^{60}Fe decay should be highest. We will then measure the nickel isotope composition of the chondrules' constituent phases, with the NanoSIMS and, provided evidence for ^{60}Fe was found, the Chicago Instrument for Laser Ionization (CHILI, which can measure all nickel isotopes simultaneously, avoids problems related to isobaric interferences, and has a better nickel sensitivity, than the NanoSIMS; [3]).

[1] Mostefaoui, S. et al. (2005) ApJ 625, 271–277.

[2] Tang, H. & Dauphas, N. (2012) EPSL 359–360, 248–263.

[3] Trappitsch, R. et al. (2018) GCA 221, 87–108.

The stable tungsten isotope composition of seawater and Mn-rich sediments from the Baltic Sea

Kurzweil*, F., Archer, C., Wille, M., Schoenberg, R., Münker, C., Dellwig, O.
*Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher Str. 49b, 50674 Köln, Germany
fkurzwei@uni-koeln.de

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

We present the first stable W isotope data of a sedimentary sequence from the Landsort Deep, Baltic Sea, covering the last ~1,700 yrs. Within this funnel-shaped basin distinct vertical stratification causing bottom water euxinia alternated with fully oxic/hypoxic conditions. During oxic periods, e.g. little Ice Age, detrital W and Mn components dominate and $\delta^{186/184}W$ are close to the upper mantle value of +0.085±0.019‰ [3]. Sediments deposited during periods of hypoxia are authigenically enriched in W and Mn and show higher $\delta^{186/184}W$ up to +0.226‰, although Mn-oxides preferentially adsorb light W. These heavy signals might result from even heavier seawater $\delta^{186/184}W$, as also indicated by our first analyses for South Atlantic seawater (+0.545±0.051‰). Our results contribute to the understanding of stable W isotope systematics in modern marine sedimentary settings, which is required to establish stable W isotopes as a potential tracer for Early Earth environmental reconstructions.

[1] Kashiwabara et al. (2017) GCA 106, 364-378.

[2] Mohajerin et al. (2016) GCA 177, 105-119.

[3] Kurzweil et al. (2019) GCA 251, 176-191.

Investigation of nitrides in chondritic meteorites: Potential records of early solar nebula processes?

Leitner*, J., Vollmer, C., Harries, D., Kodolányi, J., Ott, U., and Hoppe, P.
*Max Planck Institute for Chemistry, Particle Chemistry Dept., Hahn-Meitner-Weg 1, 55128 Mainz, Germany
jan.leitner@mpic.de

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

[1] Russell S. S. et al. (1995) Meteoritics 30, 399.
[2] Grady M. M. & Pillinger C. T. (1993) EPSL 116, 165.
[3] Weisberg M. K. et al. (1988) EPSL 91, 19.
[4] Weber D. et al. (1994) Meteoritics 29, 547.
[5] Grokhovsky V. I. (2006) MAPS 41, A68.
[6] Meibom A. et al. (2007) ApJ 656, L33.
[7] Harries D. et al. (2015) Nat. Geosci. 8, 97.
[8] Barth M. I. F. et al. (2016) MAPS 51, A154.
[9] Leitner J. et al. (2018) GCA 235, 153.
[10] Füri E. & Marty B. (2015) Nat. Geosci. 8, 515.
[11] Kung C.-C. and Clayton R. N. (1978) EPSL 38, 421.

Isotopic and petrographic characteristics of sulfides in Eoarchean peridotites from southern West Greenland

Lewis, J.A.[1,*], Hoffmann, J.E.[1], Schwarzenbach, E.M.[1], Strauss, H.[2], Whitehouse, M.J.[3], Schwarz, A.[1], Vrijmoed, J.C.[1], Münker, C.[4], Rosing, M.T.[5]
[1]Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, D-12249 Berlin, Germany
[2]Institut für Geologie und Paläontologie, Westfälische Wilhelms-Universität Münster, Corrensstr. 24, D-48149 Münster
[3]Department of Geosciences, Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden
[4]Institut für Geologie und Mineralogie, Universität zu Köln, Köln, Germany
[5]University of Copenhagen, Section for Geobiology, Øster Voldgade 5-7, 1350 København K, Geologisk Museum
*jonlewis1@zedat.fu-berlin.de

Competing hypotheses remain concerning the geodynamic setting of the formation of the first continental crust on Earth between 3.6 and >4.0Ga. In order to further our understanding of the development of continental crust and constrain the timing of the onset of modern-style plate tectonics, we performed bulk rock multiple sulfur isotopic and petrographic analysis of 3.8Ga mantle peridotites from southern West Greenland. $\Delta^{33}S$ values between -0.006 and 0.209 were observed, suggesting that surface derived sulfur subject to mass independent fractionation caused by photolytic processes in the Archean atmosphere was introduced to these peridotites. $\Delta^{33}S$ values display a positive correlation with forsterite content in olivine, a proxy for depletion, in peridotites with forsterite concentrations typical of pristine mantle. This suggests that prior to the introduction of surface derived sulfur, the peridotites were variably depleted, with the most highly depleted rocks most susceptible to isotopic overprinting. Additionally, Acid Volatile Sulfur (monosulfide fraction) $\Delta^{33}S$ values display a strong negative correlation with scandium concentrations, a proxy for melt overprint, suggesting two events introducing monosulfide sulfur: an early event in which subduction-derived fluid introduced sedimentary sulfur with a positive $\Delta^{33}S$ composition and a subsequent melt overprint event that mixed sulfur from the initial source with sulfur with a zero or negative $\Delta^{33}S$ composition. Scanning electron microscopy and electron microprobe analyses of sulfide grains reveal a dominance of pentlandite and pyrrhotite, consistent with a mantle origin. The sulfides are crosscut by secondary minerals (e.g., amphibole, serpentine) representing metamorphism and serpentinization that occurred after any potential subduction-related introduction of mass independently fractionated sulfur. This suggests that the sulfides may have originally crystallized out of subduction-related fluids in the Eoarchean. Multiple sulfur and lead isotopes of individual sulfide grains in these and other intrusive and extrusive rocks of Archean age from southern West Greenland will be measured by SIMS as part of future work, in order to confirm the age of the sulfides and determine whether and to what extent isotopic composition varies between sulfide grains.

The Trace Element Composition of a Range of Modern and Archean Microbial Carbonates

Martin*, A. N., Unruh, C.S., Lazarov, M., Markowska, M., Junginger, A., Bischoff, K., Chivas, A.R, Weyer, S.
*Institut für Mineralogie, Leibniz Universität Hannover, Callinstraße 3, Hannover, Germany.
a.martin@mineralogie.uni-hannover.de

Archean microbial carbonates represent some of the earliest evidence for life on Earth and are valuable geochemical archives for the redox state of early waterbodies. Here we analyse the trace element composition of microbial carbonates from modern and Archean samples by fs-LA-ICPMS to target specific petrographic components. In modern and ancient samples, all elements except Sr are correlated to at least some degree with Th, which is attributed to detrital input. Principal Components Analyses suggest that the enrichment of redox-sensitive metals varied in different samples, e.g. microbial carbonates from a marine-influenced hypersaline lake (Lake Baghdad, Rottnest Island, WA) were enriched in U, Ni, Co, Mo, Fe, V, Mn but those from a freshwater volcanic lake (Lake Chew Bahir, Ethiopia) were enriched in Mn, La, and Ni with minor enrichments in Co and V. Similar to modern samples, the Archean sample (Tumbiana Formation) was also enriched in Fe, Ni, and Co (with minor enrichments in V); however, unlike modern samples, these redox-sensitive elements are inversely correlated with Mn, La and Ce. This inverse correlation may reflect the fundamentally different redox conditions in which the Tumbiana Formation formed. The shared enrichment of Fe, Ni, and Co in modern and ancient microbial may serve as an indicator for the biogenicity of ancient carbonates.

Radiogenic tungsten isotope variations in the ca. 3.53 Ga Theespruit Formation, Barberton Greenstone Belt, South Africa

Messling*, N., Willbold, M., Hegner, E.
*Geowissenschaftliches Zentrum, Abt. Isotopengeologie, Goldschmidtstraße 1, 37077 Göttingen, Germany
nils.messling@uni-goettingen.de

Differentiation of Earth into a metallic core and a silicate mantle as well as the onset of modern-style mantle convection are probably amongst the most pervasive transformations our planet has endured. These early planetary-scale processes were essential in converting the Earth into a habitable realm: On its surface, the Earth's intricate internal geodynamic system leads to the formation of rift systems and subduction zones. Yet, how and when modern-style mantle convection evolved within the first billion years after the accretion of the Earth remains enigmatic. Addition of meteoritic material during the late stages of Earth's accretion replenished the Earth's mantle with elements that previously sequestered into the core during its formation. These siderophile elements can be used as tracers, constraining the timing of mantle homogenisation. Here, we present ^{182}W isotope data for rocks of the Theespruit Formation, that represent the oldest supracrustal rocks in the Barberton supergroup with an age of ca. 3.55- 3.52 Ga. The succession mainly consists of strongly deformed mafic-ultramafic metavolcanics rocks and layers of dacites and rhyolites as well as felsic schists. Although the rocks of the Theespruit Formation overlie the Sandspruit Formation, the exact field relations between the two formations remain enigmatic and might represent a single lithostratigraphic unit. The basal Theespruit- Sandspruit Complex is infolded into the TTGs of the Stolzburg Pluton and has been metasomatized and metamorphosed under amphibolite-facies conditions. Trace elements analysis of the felsites indicate a metabasaltic protolith [1] whereas older zircon xenocrysts and a range of εHf in magmatic zircons imply derivation from older crustal rocks as well as a mantle origin [2]. In this study we analysed freshly crushed samples of 22 felsic rocks of the Theespruit Formation to test if the source of these rocks derived from a well-mixed mantle or rather one, that has not fully incorporated the late accreted material. An incomplete mixing of this 'late veneer' material is already indicated by low abundances of highly siderophile element in rocks of basal members in the Barberton Greenstone Belt[3].

[1]Furnes, H. et al. (2013) Gondwana Research 23, 403–428.

[2]Kröner, A. et al. (2016) Precambrian Research 279, 123–143.

[3]Maier; W. D. et al. (2009) Nature 460, 620–623.

Volatile organic compounds in 3.5 Ga old barite-hosted fluid inclusions: a substrate for early microbial life?

Mißbach*, H., Duda, J.-P., van den Kerkhof, A.M., Pack, A., Reitner, J., Thiel, V.
*Geobiology, University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen, Germany, hmissba@gwdg.de

The c. 3.5 Ga Dresser Formation of the East Pilbara Craton (Western Australia) contains large amounts of blackish barites that release an intense H_2S smell when crushed. These barites are typically interbedded with sulfidic stromatolites. Petrographic analysis and microthermometry revealed the presence of abundant primary (i.e. syngenetic) fluid inclusions in the blackish barites (aqueous-carbonic-sulfuric and non-aqueous carbonic-sulfuric). Raman spectroscopy and gas chromatogaphy-mass spectrometry independently demonstrated the presence of various indigenous low molecular weight compounds in the entrapped fluids (e.g., H_2O, H_2S, COS, CO_2, CH_3SH, CS_2, CH_4, various polysulfides). We propose that seepage of these compounds fueled microbial life in hydrothermal settings during Dresser times, providing a fertile substrate for stromatolite growth. Ongoing studies on fluid inclusions and associated minerals in the Dresser barites will help to further validate this hypothesis.

A critical view on Raman spectroscopy of organic matter using Archean and Proterozoic samples

Nabhan, S.*, J., van Zuilen, Kah, L.C., M.A., Heubeck, C.
*Universite de Paris, Institut de Physique du Globe du Paris, CNRS, F-75005 Paris, France
nabhan@ipgp.fr

Raman spectroscopy of organic matter (RSOM) is an important tool in geosciences and specifically in the exploration of the emergence and evolution of early life. In meta-sedimentary rocks, RSOM is commonly used to estimate maximum metamorphic temperatures while in sedimentary rocks (with lower thermal overprint) it is used together with FTIR to differentiate between organic precursors (e.g. prokaryotes vs. eukaryotes).

We tested the reliability of RSOM as geothermometer for meta-sedimentary rocks on samples from the ca. 3.22 Ga old Moodies Group, BGB, South Africa. The age and simple quartz-rich sandstone composition with abundant fossilized microbial mats allows to avoid disturbances such as detrital organic material (OM) with a higher thermal overprint. Results show that the overall dependence of maturation of OM on the degree of thermal overprint is limited. Rather, inclusions of OM <5 µm in diameter hosted in recrystallized chert and dolomite show a Raman signal that systematically indicates a temperature 50 – 80°C higher than that calculated from nearby OM in the sandstone matrix of the same thin section.

Black cherts from the ca. 1.1 Ga old Angmaat Formation, Bylot Supergroup, Baffin Island, contain numerous coccoidal and filamentous microfossils of various taphonomic grades although the majority of OM is preserved as homogenized material that does not allow the recognition of microfossils. Raman spectra from individual microfossils are highly variable and suggest a thermal overprint from < 150°C to ca. 280°C. These variations are observed between samples and also on a microscopic scale between neighboring microfossils, independent of their taxonomy and taphonomy. Homogenized OM, however, shows a homogeneous Raman signal across the whole set of samples that corresponds to the lowest-mature (< 150°C) microfossils. This implies that variations of the Raman signal of low-mature OM are more dependent on the diagenetic context than on organic precursor material.

This Raman study of maturation pathways of organic material in Precambrian rocks shows that several processes must be considered in both the metamorphic and the diagenetic realm, as causes of significant variations of the Raman signal of organic material in rocks.

Heterogeneities in Earth’s mantle over time due to melt depletion and mineral phase transitions

Noack*, L., Balduin, A.
*Freie Universität Berlin, Malteserstr. 74-100, D-12249 Berlin, Germany
lena.noack@fu-berlin.de

The local composition of Earth’s mantle changes over time mainly due to melt extraction, subduction of crustal material, and inefficient mantle mixing. In the Archean, mantle temperatures exceeded present-day values by ~150-200 degrees, which affected the phase transition from upper to lower mantle, such that material mixing between these layers may have been reduced. We investigate how unknown early Earth mantle conditions may have influenced the phase transition Clapeyron slopes and hence global mantle convection and mixing.

We find that under Archean conditions, the upper mantle becomes more and more depleted, while the lower mantle stays primordial in composition for a long time span. The reason for this evolving heterogeneity is that the lighter harzburgite material resists transportation to the lower mantle at to the ringwoodite-perovskite phase transition. A cooler mantle together with the initiation of plate tectonics can later lead to more efficient mixing of Earth’s upper and lower mantle.

Feasibility of plate tectonics during the Archean: Insights from 3D numerical thermo-mechanical modelling

Andrea Piccolo[1], Nicholas Arndt[2], Richard White[3], and Kaus Boris[1] [1]
JGU Mainz, Institute of Geosciences, Department of Chemistry, Pharmacy & Geosciences, Mainz, Germany
piccolo@uni-mainz.de

Slab-pull forces are considered the major driving forces of the present-day plate tectonic. Their efficiency relies on the buoyancy contrast between asthenosphere and subducting plate and on the strength of the latter. Subduction is not only pivotal for understanding the dynamics of plates but also represents the only modern geodynamic setting that produces significant amount of juvenile continental crust and allows exchange between the mantle, lithosphere and atmosphere.
One of the most important unsolved questions is related to the onset of plate tectonics, which is inherently linked to feasibility of the subduction during the early in Earth history. During the Archean, the mantle potential temperature was higher than nowadays, which promoted extensive mantle melting and possibly a weaker lithosphere. The intense magmatism associated with the high mantle potential temperature generated highly residual lithospheric mantle that was more buoyant than the underlying asthenosphere. Altogether these factors may have inhibited the dynamic effect of slab pull and prevented modern style tectonic during the Archean. However, the Archean mantle potential temperature is still not well constrained, and many of these theoretical considerations have not been fully tested by integrating petrological forward modelling into 3D numerical geodynamic modelling.
In our contribution, we focus on the feasibility of modern style plate tectonic as a function of the mantle potential temperature and the composition and structure of the lithosphere. We compute representative phase diagrams that represents the composition of mantle lithospheric and its complementary crust as a function of the mantle potential temperature and integrate them into large-scale 3D numerical experiments. The numerical setup is constructed assuming the existence of a set plates interacting with each other. We prescribe the principal plate boundaries and allow the model to spontaneously evolve as function of the thermal ages of the prescribed plate, testing the effect of continental terrains and oceanic plateau on overall geodynamic evolution. The overall goal is to understand the feasibility of plate tectonics at high mantle potential temperature and to estimate the amount of fluid released by the subduction processes, which provide useful insights on the formation of continental crust.

The role of early Archean Terrestrial Environments in Weathering, Sediment Transport, and the Colonization of Land

Reimann, S.*; Janse van Rensburg, D.*; Heubeck, C*
*Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, 07749 Jena, Germany
sebastian.reimann@uni-jena.de

Archean terrestrial strata, especially in the Moodies Group of the Barberton Greenstone Belt, South Africa and Eswatini, preserve a unique and valuable depositional record which allows to constrain the history of interaction between geo-, bio- and atmosphere. This includes the conditions of paleosol formation, the intensity and type of weathering, and processes of sediment generation and maturation. The oldest preserved (microbial) traces of early life on land bear on fundamental geo-bio-interactions such as metabolism and degree of nutrient delivery, strategies of radiation avoidance, communities and symbioses, and atmospheric composition. Eolian strata may convey unique environmental parameters such as local wind strength and atmospheric density, with implications for aridity and circulatory systems. Lastly, terrestrial evaporites relate to temperature, evaporation and groundwater movement.
Our work in the Moodies Group to date has documented (1) different morphotypes of microbially influenced sediments (including stromatolites); (2) extent of floodplain-facies evaporitic gypsum concretions; (3) thick large-scale and coarse-grained cross-bedded sandstones, which were described as eolian but are likely deltaic; (4) trough-cross-bedded fluvial sandstones with interfluve ponds; and (5) proximal-alluvial conglomeratic debris flows.
We will use geological (mapping, section measuring, textural studies, petrography) and geochemical (whole-rock geochemistry, mass spectrometry) tools to constrain terrestrial depositional parameters and the habitats of marginal marine and terrestrial microbial communities. This may allow to infer conditions on early Mars where aqueous environments were (and are) far more tenuous.

Putative Tsunami Deposits in the 3.5 Ga Dresser Formation (Pilbara, Western Australia)

Runge, E; Mißbach, H; Duda, J.-P.; Reitner, J.*
*Geobiology, University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen, Germany
jreitne@gwdg.de

The establishment of Earth's earliest life in near surface environments is closely linked to the depositional mechanisms in its habitats. Deciphering the sedimentary dynamics on early Archean shelves, especially during catastrophic events, may therefore yield important clues to the nature of these habitats.
However, well preserved Paleoarchean sediment successions are rare and usually consist of chemical sediments (e.g. chert) and volcanoclastic material. Here we report a ca. 100 m long and 5 - 6 m thick channel fill deposit, incising the ca. 3.5 Ga North Star Basalt near the Old Dresser Mine, Eastern Pilbara Craton. The unit consists of bedded cherts, brownish mostly laminated carbonates and jaspilitc chert. The most striking feature of this section is a succession of two subsequent massflow layers, each consisting of pebble-sized imbricated chert clasts, followed by laminated and graded carbonate sediment. The basal chert clasts in these massflow layers display a mirrored imbrication, indicating a switch in transport direction during the event. For now, we interpret this sequence as a tsunami event with accompanying carbonate turbidite deposition, possibly triggered by an impact event or heavy earthquake. The reflection of the wave on a coastal area may explain the mirrored clast imbrication (onflow *versus* backflow), while the thick carbonate deposits indicate widespread marine carbonate production.

Which tectonic model of the Barberton Greenstone Belt fits regional stratigraphic and structural data best?

Matthias Schmitz*, Christoph Heubeck
Department of Geosciences, Friedrich-Schiller-Universität Jena
* now at: SST Consulting, Aachen

The Barberton Greenstone Belt (BGB) and its surroundings feature prominently in the debate about Archean tectonic processes because this geologic region is of substantial size, structurally coherent, well exposed and well investigated. It has the potential to provide a detailed geological record and general insights of the transition from the pre-plate-tectonic mode to modern-style plate tectonics. A variety of actualistic and non-actualistic contradictory tectonic settings, including gravitational collapse, terrane accretion, foreland basin, continental rift, passive margin, doubly-vergent subduction and partial convective overturn settings have been proposed. We compiled published data from those studies and compare their predictions to own field observations.
We conclude that none of the models can account for all of the major structural features nor can they adequately explain the heterogeneous timing and pattern of deformation in the BGB. However, the partial convective overturn model, despite some weaknesses and oversimplifications, appears to be suited best to explain the geometry and orientation of the dominating structural element of the BGB, the tightly folded, vertically plunging Onverwacht Anticline (OA) with its >8 km thick limbs. Subsidence caused by gravitationally induced sinking of dense (ultra-)mafic greenstones into a hot and buoyant felsic lithosphere, resulting first in tight folding and then near-contemporaneous block rotation into the vertical, may explain the origin of this large structure. The unusual fold style of the greenstone belt adjacent to the OA can largely be considered as a consequences of space problems to the rise and rotation of this large structure. In comparison to the 10s-of-km vertical displacement, greenstone belt-wide (sub-)horizontal shortening appears to have played only a subordinate role in this enormous redistribution of mass in the early Archean lithosphere, except along the regionally highly strained southern BGB margin in Eswatini.

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

Schwarz*, W.H., Schmitt, A.K., Trieloff, M.
*Institut für Geowissenschaften, Universität Heidelberg, INF 234-236, D-69120 Heidelberg, Germany
winfried.schwarz@geow.uni-heidelberg.de

The first 500 Million years of the solar system are a critical period during which life emerged on Earth. Detrital zircon recovered from a handful of locations worldwide are the only tangible materials of this period when a habitable surface became established. Graphite inclusions in these zircons have been interpreted to contain C isotopic signatures for biologic activity with $\delta^{13}C_{PDB}$ = -24 ± 5 ‰ already by 4.1 Ga [1], but how graphite entered magmatic zircon and was preserved since then remains incompletely understood. To interpret the rich record of Hadean zircon inclusions requires a better understanding of how the near-surface C-cycle interfaces with the magmatic environments where zircon crystallized and may have entrapped graphite. We employ spatially resolved C-isotopic analysis of graphite-bearing granites as a potential analogue for the environment where Hadean zircon formed, and investigate how the biologically derived C is transferred into zircon grains.

In a first step, sample preparation procedures were established to avoid C contamination. Where epoxy contamination cannot be completely avoided during mounting, we found that it can be monitored during SIMS analysis by detection of $^{12}C^{1}H_2$. A secondary reference material for C isotope analysis was characterized because primary references like USGS24 graphite ($\delta^{13}C_{VPDB}$ = -16.049 ± of 0.035‰ [2]) are only homogeneous at the scale of bulk analysis. SIMS analyses on USGS24 yielded an internal precision of only ~ 0.9 ‰, indicating heterogeneity at the resolution of the SIMS ion beam spot diameter of ~1-2 µm. Moreover, with SEM analyses sample impurities were detected in USGS24. We characterized carbonaceous material GR961 (Sri Lanka, Heidelberg collection) by Raman and SEM and confirmed that it is pure graphite. SIMS analyses of GR961 (using USGS24 as primary standard) yielded a $\delta^{13}C_{VPDB}$ value of -5.60 ± 0.16 ‰ (internal precision). Bulk analyses of GR961 are pending.

[1] Bell, E.A. et al. (2015) PNAS, 112(47), 14518-14521.

[2] Gonfiantini, R. et al. (1995) IAEA-TECDOC-825. International Atomic Energy Agency, Vienna, Austria, 13-29.

Carbon destruction and C/O ratios in the inner solar nebula and other planet-forming disks

Semenov[1,*], D., Molyarova[2], V. Akimkin[2], T., H.-P. Gail[3], Th. Henning[1]
[1]Max Planck Institut für Astronomie, Königstuhl 17, D-69117 Heidelberg
[2]Institute of Astronomy, Russian Academy of Sciences, 119017, 48 Pyatnitskaya st., Moscow, Russia
[3]Institut für Theoretische Astrophysik, Universität Heidelberg, Albert-Ueberle-Str. 2, 69120 Heidelberg, Germany
*semenov@mpia.de

The variations in the volatile content and C/O ratios in the inner solar nebula have been imprinted into the properties of terrestrial and giant planets of the solar system. The physical evolution of the nebula, along with plethora of complex chemical processes, have been driving chemical reprocessing of gaseous molecules, ices, refractory materials and carbonaceous grains, leading to very carbon-poor Earth. Similar processes could be happening in other planet-forming disks studied now by astrophysicists. In this study, we aim to better understand how high temperature processes, UV, X-rays and CRPs as well as chemical destruction of refractory CHON material and solid carbonaceous grains affects the composition of the gas, ices and refractory carbon in the young solar nebula and similar disks around various pre-main-sequence stars. For that, we use the 1+1D ANDES2 disk physical model coupled with the time-dependent gas-grain ALCHEMIC chemical model and follow the evolution of the refractory carbon and C/O ratios for a grid of protoplanetary disks surrounding T Tauri and Herbig Ae stars. We show the spatial distributions of the major C- and O-bearing gas-phase molecules and ices, and discuss their key formation pathways. We find that the local C/O ratios in the gas and ice phases can significantly deviate from the initial elemental C/O ratio, in particular, when destruction of refractory carbon and CHON material in the very inner nebula region, <2–3 au, is considered. The extent of the carbon-poor reservoir and the degree of the solid carbon depletion as well as C/O variations sensitively depend on the properties of the star and the disk as well as initial abundances. By tuning poorly constrained chemical data for destruction of carbon grains and refractory CHONs by O, OH and O_2, we could significantly reduce the amount of refractory carbon in the zone of terrestrial planet formation already in the very young solar nebula, before the onset of planetesimal formation (see Fig. 1 below).

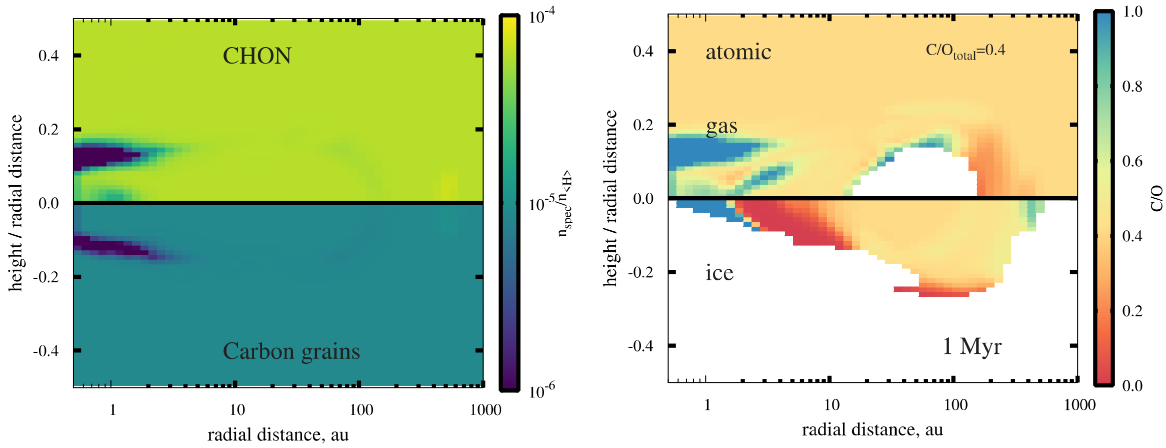

Fig 1.: *(Left panel) The radial and vertical distribution of the relative abundances of the refractory CHON material (upper half) and solid carbonaceous grains (lower half) in the solar nebula at 1 Myr. The efficient destruction of solid carbon occurs in the upper, UV-irradiated layers only, with plenty of OH and O. In contrast, the CHON material, which is the dominant source of refractory carbon in the model, is also partly destroyed in the midplane at <3 au. (Right panel) The radial and vertical distribution of the C/O ratios for the gaseous species (upper half) and ices (lower half) at 1 Myr in the same model. The release of refractory carbon to the gas due to the carbon destruction increases the C/O ratios in the inner nebula to a value of ~ 1.*

182W isotope patterns in mantle derived and crustal rocks from the Pilbara Craton, NW Australia

Jonas Tusch[1], Carsten Münker[1], Mike Jansen[1], Eric Hasenstab[1], Chris S. Marien[1], Florian Kurzweil[1], Martin van Kranendonk[2]

[1]Universität zu Köln, Germany; [2]Australian Center for Astrobiology, University of New South Wales, Australia
jonastusch@gmx.de

The record of ^{182}W isotope anomalies in terrestrial rocks has recently been expanded from the Archean to the Phanerozoic. Unfortunately, most ^{182}W isotope studies only provide "snapshots" of the early terrestrial rock record and do not consider elemental W redistribution by secondary processes that would also affect ^{182}W isotope systematics. This might obscure the original W isotope composition of parental mantle sources and can complicate the reconstruction of the secular ^{182}W isotope evolution.

Here, we atttempt to assess the long-term evolution of ^{182}W isotope patterns during the Archean by studying mantle-derived and crustal rocks from the Pilbara Craton, NW Australia. Mantle-derived rocks provide snapshots of the ambient mantle composition, whereas the crustal rocks provide a long-term average of crust-mantle evolution. By combining ^{182}W isotope analyses with high-precision isotope dilution measurements for HFSE, U, and Th, we demonstrate the preservation of primary geochemical signatures in our sample selection, which allows for the reconstruction of the ^{182}W isotope composition of the ambient mantle in NW Australia. Mantle-derived rocks from the oldest Warrawoona Group display uniform excesses and define a mean $m^{182}W$ of +12.1 ± 2.1 ppm (95% CI). Younger rocks from the the Kelly and Soanesville groups document that ^{182}W isotope anomalies decrease between 3465 and 3340 Ma to ca +5 ppm and vanish by c. 3190 Ma. Diminishing ^{182}W isotope anomalies in the Pilbara Craton are also archived in shales and granitoid rocks, which provide an integration of the lithosphere. These rocks are characterized by a lower ^{182}W isotope anomaly of + 8.0 ± 1.2 ppm (95% CI). Similar to the evolution of mantle-derived rocks, anomalies in granitoids slightly decrease with decreasing age and are higher in less evolved rocks. The origin of elevated ^{182}W isotope compositions in Pilbara rocks, and their decline to modern mantle values, is consistent with a progressive in-mixing of late veneer material, as previously suggested by decreasing PGE depletions in rocks from the same lithostratigraphic units [1].

[1] Maier et al. (2009) *Nature* 460, 620-623.

Preservation of microbial communities in siliceous sinters of terrestrial hydrothermal systems: natural laboratories for biosignature preservation in ancient silicified deposits.

van Zuilen*, M.A., Wilmeth, D., Nabhan, S., Myers, K.D., Gong, J., Slagter, S., Grandin, P., Couasnon, T., Mand, K., Lalonde, S.V., Sansjofre, P., Homann, M., Konhauser, K., Munoz, C.
*Universite de Paris, Institut de Physique du Globe du Paris, CNRS, F-75005 Paris, France
vanzuilen@ipgp.fr

Silica sinters are surface expressions of geothermal activity, produced when amorphous silica (opal-A) precipitates via cooling and evaporation of hot, silica-supersaturated groundwater discharged by hot springs and geysers. Microorganisms (predominantly cyanobacteria and chloroflexi) are ubiquitously present in these settings, their cell surfaces and extracellular polymeric substances (EPS) acting as templates for silica precipitation, generating sinters with various laminated stromatolitic morphologies, palisade fabrics, fenestra, and molds that are often interpreted as biosignatures that can be traced in silica deposits throughout the early rock record. The preservation of these biosignatures depends strongly on the efficiency of initial silica entombment, biological degradation, dewatering, diagenesis, and ultimately metamorphic recrystallization. It is currently poorly understood whether certain microorganisms or certain microbial components are better preserved than others, creating a bias in the rock record. Silica mounds can be used as natural laboratories to study the relative degradation of various microbial cells and their extracellular polymeric substances. Here we present an overview of our recent studies of active and extinct silica mounds in the El Tatio geothermal field, Chile. We show how communities of sheathed cyanobacteria are effectively silicified, and subsequently degraded while their protective sheaths create molds, macroscopic pore networks, and palisade fabrics that survive in artificial diagenesis experiments. In contrast, unsheathed microorganisms are degraded at an early stage of alteration [1]. In order to study the complete dynamic interplay of biological, sedimentary, and geochemical processes that act on the preservation of biosignatures in a geothermal system through time, we have recently obtained several drill cores (1-6 m depth) through silica sinter at increasing distances from an extinct vent source at El Tatio. Radiocarbon ages indicate sinter deposition ~13 to 10 ka before present, initiating on glacial sediments. The cores exhibit several broad lateral and vertical trends, showing how microbial fabrics are particularly well preserved in the vent-distal, cooler zones. Microbial and detrital fabrics become more abundant in the top 0.5 m of all cores, indicating gradual cooling before termination of the local vent system [2]. Lateral and vertical variations in opal-A and opal-CT occur, showing how secondary fluid alteration has affected the system. Overall, these studies on modern and recently extinct sinter mounds provide a good framework for future geobiological studies of modern and ancient hydrothermal environments.

[1] Gong, J. et al. (2019) *Astrobiology* 20 (published online 30/10/2019).

[2] Wilmeth, D., et al. (in prep) Sedimentary Geology.

The fate of volatiles during magma body crystallization on early Earth

Vulpius1*, S., Noack1, L., Sohl2, F., Ortenzi2, G., Hoffmann1, J.E.
1Freie Universität Berlin, Institute of Geological Sciences, Malteserstr. 74-100, D-12249 Berlin, Germany
2German Aerospace Center (DLR, Institute of Planetary Research, Rutherfordstr. 2, D-12489 Berlin, Germany
sara.vulpius@fu-berlin.de

Outgassing is the main volatile source of the Earth´s atmosphere. In the Hadean and Archean, this atmosphere was essential for the origin and evolution of life. However, it´s buildup and composition remains uncertain and requires further investigation. The volatiles contributing to the development of the atmosphere are released form either an extrusive or an intrusive magma system. At least today, intrusive magma rates are considerably higher compared to extrusive rates. While some studies regarding outgassing from extrusive systems already exist, the volatile release from intrusive magma bodies is often neglected. The reason is the increasing solubility of volatiles (like H2O or CO2) with increasing pressure. Therefore, at greater depths the volatiles do not exsolve from the melt and no outgassing is expected. However, ongoing crystallization of a magma body due to cooling leads to an enrichment of incompatible elements in the melt, as they cannot be incorporated into the crystal lattice. Since H2O or CO2 are highly incompatible, they accumulate in the remaining melt until the saturation level is exceeded and they exsolve form the melt. The released volatiles can subsequently ascent due to cracks or fissure, to reach the surface and contribute to the buildup of the atmosphere.

We model the content and speciation of volatiles released from intrusions, emplaced at different depths within the lithosphere. To simulate the crystallization of the magma body we use the batch melting equation and calculate the temperature depending on the pressure. Subsequently, we compute the solubility and the amount of degassing for a basaltic melt composition, since on early Earth melts are suggested to be primarily mafic. The oxygen fugacity is also considered. In the model, we vary the initial volatile content in the melt, the pressure, the temperature and the partition coefficient for the relevant molecule. To benchmark our results, we use literature values of basalts and melt inclusions. Additionally, we investigate the likelihood of reactions with the surrounding mantle, to form water-bearing minerals, during the ascent of volatiles. Finally, we compare our results with studies on extrusive outgassing to determine the impact of intrusive degassing on the build-up and composition of the atmosphere.

Analyses of extraterrestrial samples using quadrupole ICP-MS

Wombacher*, F., Abouchami, W., Bischoff, A., Braukmüller, N., Galer, S.J.G., Kaufmann, L., Münker, C.
*Institut für Mineralogie and Geologie, 50674 Köln, Germany
fwombach@uni-koeln.de

The elemental compositions of planetary materials provide fundamental insight into the processes that lead to their formation. Here, major and trace element abundances in carbonaceous and enstatite chondrites and in lunar samples were determined using an iCap quadrupole ICP-MS. Quantification was based on matrix matched calibration and Rh and Re internal standards. For some samples, volatile elements (Cu, Zn, Ga, Ag, Cd, In, Sn and Tl) were also determined by isotope dilution following chemical separation [1].

For chondrites, 56 elements were determined via external calibration. Nine replicates for the Allende Smithsonian reference powder yielded relative 2 standard deviations typically much better than 5% (9% for Se; 14% for Be). Results agree with Allende reference data within 10% for 47 elements, while data for Sn, Lu, Th, Cs, W, Pb, Ag, Be and Ga differ by 12 to 41%. Most data for a duplicate digestion of the Allende Smithsonian powder agree within a few percent, except for six elements which deviate by up to 15%.

The elemental compositions of ungrouped desert finds (Acfer 094 C2, Sahara 0182 C3, DaG 056 C3 and HaH 073 C4) were found to be very similar to that of CM2 or CV3/CO3 chondrites, but the latter three exhibit a stronger depletion of Tl, In and Cd. The previous observation, that CI normalized abundances of volatile elements with condensation temperatures between 800 and 500 K form plateaus at different levels for different carbonaceous chondrite groups [2], is corroborated by new data for C2, CM, CR, CO and CV chondrites as well as by isotope dilution analyses of volatile elements for Orgueil, Murchison and Allende.

Enstatite chondrites display more complex fractionation patterns than carbonaceous chondrites. Siderophile and alkali elements are enriched, while chalcophile elements are depleted. (Ultra-)refractory lithophile elements are more depleted in EH than EL samples. The plateau volatile elements as defined for carbonaceous chondrites are also clearly distinct in enstatite chondrites, but S and Se tend to be more abundant than the other “plateau elements” and some of the most volatile elements Cs, In, Cd and Tl tend to be more depleted especially in EL samples.

Isotope dilution applied to six Apollo samples [see 3] reveal comparatively high volatile element abundances in three soil samples, including orange glass soil 74220. Ferroan anorthosite 60025 displays high abundances for the most volatile elements In and Tl, while impact melt breccia 65015 and basalt 70017 display the strongest depletions. External calibration ICP-MS yields reasonable agreement with isotope dilution data for Cu, Cd, In and Tl and with much of the available literature data.

[1] Braukmüller et al. (2020) GGR submitted.

[2] Braukmüller et al. (2018) GCA 239, 17-48.

[3] Abouchami et al. (2020), this meeting.

Paleoarchean carbonates – important archives for reconstructing early Earth's environments

Xiang, W., Duda, J.-P., Pack, A., Willbold, M., Reitner, J.
*Georg-August-Universität Göttingen, Goldschmidtstr. 3, D-37077 Göttingen, Germany
jreitne@gwdg.de; wanli.xiang@geo.uni-goettingen.de

Early Archean carbonates from the Pilbara Craton (Western Australia) and the Barberton Greenstone Belt (South Africa) occur in a variety of facies. In the Pilbara, these facies include ca. 3.5–3.4 Ga old pillow-basalt interspaces (North Star Basalt, Mt. Ada Basalt, Apex Basalt, Euro Basalt), ca. 3.5 Ga old hydrothermal vein and bedded cherts (Dresser Formation), ca. 3.4 Ga old stromatolites (Strelley Pool Formation). The carbonates exhibit variable mineralogies, ranging from calcite, through dolomite to Mn/Fe-rich dolomite (ankerite/kutnahorite). The carbonates were formed *via* the following pathways:

1. Abiotic precipitation: Carbonates in pillow-basalt interspaces precipitated abiotically from highly alkaline brine solutions as indicated by $\delta^{13}C$-values (ca. 0±1‰), $^{87/86}Sr$ ratios (0.701467–0.705710) and REE+Y signatures. Their formation was linked to intense hydrothermally driven pumping of seawater through the oceanic crust – likely a significant sink for CO_2 in Archean seawater.
2. Organomineralization *sensu* [1]: This carbonate formation pathway is evidenced by an intimate association between mineral precipitates and organic matter. Two groups can be distinguished:
    a. Fine-grained sedimentary carbonates in the Dresser and Strelley Pool Formations. These include dolomites and calcites which precipitated from seawater with elevated alkalinity as indicated by $\delta^{13}C$-values (ca. 1–2‰).
    b. Carbonate crystals in bedded cherts of the Dresser Formation. These include kutnahorite and other dolomitic carbonate minerals that precipitated in low temperature hydrothermal pond environments. The hydrothermal influence is e.g. reflected in relatively low $\delta^{13}C$-values of the carbonates (ca. –6‰), indicating a magmatic/mantle origin of the CO_2. The precipitates commonly encapsulate putative microbial remains and so potentially form excellent biosignatures for testing the presence of life in ancient hydrothermal settings.
3. Microbially mediated mineralization: Stromatolites in the Strelley Pool Formation almost entirely consist of dolomites. Carbonate formation was probably coupled to anoxygenic photosynthesis as indicated by high $\delta^{13}C$-signatures (ca. +4‰) and REE+Y characteristics indicative for seawater. It appears likely that the process was already linked to microbial exopolymeric substances (EPS)

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

[1] Reitner, J. et al. (1995) Bull. Inst. Oceanography. Monaco 14, 2, 237–303.