

# Abstracts

# of the Third General Meeting

# "Early Earth evolution"

### March 21-23, 2018

## Göttingen



PROGRAMME General Meeting 2018 SPP 1833 "Building a Habitable Earth" "Alte Mensa", Wilhelmsplatz 1, Göttingen

#### Wednesday, March 21st: Early Solar System / Early Earth Differentiation I

14.00-14.15	Carsten Münker, Köln: Introductory remarks
14.15-14.30	Dmitry Semenov, München: Origin of volatiles and organics on Earth, IDPs, meteorites, and comets
14.30-14.45	Hubert Klahr, Heidelberg: Tracing back Earth building material: Identifying the perfect Ice, Dust, Pebble and Planetesimal Cocktail from simulations of the solar nebula
14.45-15.00	Frank Wombacher, Köln: Cadmium stable isotope fractionation during evaporation and recondensation at atmospheric pressure
15.00-15.15	Ninja Braukmüller, Köln: A three component model for the refractory and volatile element inventory of carbonaceous chondrites
15.15-15.30	Wladimir Neumann, Münster: Modeling the evolution of the parent body of acapulcoites and lodranites: A case study for partially differentiated asteroids
15.30-15.45	Cornelis Dullemond, Heidelberg: Modelling the origin of Earth's water within constraints by noble gas isotope systematics
15.45-16.00	Mario Fischer-Gödde, Köln: Ruthenium isotope constraints on the timing of volatile element accretion
16.00-16.45	Coffee Break
16.45-17.00	Leonid Dubrovinsky, Bayreuth: Light elements oxygen and nitrogen in the core of the habitable Earth
17.00-17.15	René Heller, Göttingen: Tidal heating in the early Earth-Moon system under a faint, young sun
17.15-17.30	Christian Maas, Münster: On the effects of planetary rotation on early Earth differentiation
17.30-17.45	Esther Posner, Bayreuth: Fate of carbon during early differentiation of the Earth
17.45-18.00	Ulrich Hansen, Münster: Double diffusive convection and Layer Formation in Planetary Mantles
18.30	optional: Joint Dinner in the restaurant "Bullerjahn" (Markt 9, at one's own expense)

Thursday, March 22nd: Early Earth Differentiation II / Onset of Plate Tectonics and Continental Crust Formation

9.00-9.15	Mario Trieloff, Heidelberg: Noble gas state of the Archean mantle			
9.15-9.30	Raul Fonseca, Köln: The behaviour of the moderately volatile elements Sn and In during partial melting and crystallization			
9.30-10.00	Elis Hoffmann, Berlin ( <b>Keynote</b> ): 'Earth's evolving differentiation history - from a primordial mantle to stable blocks of continental crust'			
10.00-10.15	Jonas Tusch, Köln: Early silicate differentiation of the Isua mantle? Insight from Tungsten isotopes and HSE abundances			
10.15-10.45	Coffee Break			
10.45-11.00	Kathrin Schneider, Berlin: The origin of komatiites and basalts of the lower Onverwacht Group, Barberton Greenstone Belt (South Africa)			
11.00-11.15	Nicholas Arndt, Grenoble: Numerical modelling demonstrates flaws in the sagduction model			
11.15-11.30	Matthias Schmitz, Jena: Large-scale fold structures of the Barberton Greenstone Belt, South Africa & Swaziland			
11.30-11.45	Sumit Chakraborty, Bochum: Insight into Archean thermal evolution using P-T-t history of mafic granulites from Coorg, India			
11.45-12.00	Elis Hoffmann, Berlin: Elucidating Eoarchean geodynamic processes using multiple S isotopes			
12.00-12.30	General Discussion			
12.30-14.00	Lunch Break			



### SPP1833 Building a

Habitable Earth

#### PROGRAMME General Meeting 2018 SPP 1833 "Building a Habitable Earth" "Alte Mensa", Wilhelmsplatz 1, Göttingen

Thursday, March 22nd: Ocean and atmosphere evolution I			
14.00-14.30	Sebastian Viehmann, Wien ( <b>Keynote</b> ): Reconstruction of the earliest marine habitats on Earth: Insights from BIFs and stromatolites		
14.30-14.45	Horst Marschall, Frankfurt: Tracing secular changes in composition of Archean oceans and continental crust through boron isotopes		
14.45-15.00	Nina Albrecht, Göttingen: High-precision measurement of $\delta^{17}O$ and $\delta^{18}O$ in carbonates by high-resolution gas source mass spectrometry – analytical setup and application		
15.00-15.15	Sukanya Sengupta, Göttingen: Triple Oxygen Isotope Study of a Mesoarchean Banded Iron Formation, Pongola Supergroup, South Africa		
15.15-15.30	Annika Brüske, Hannover: Uranium isotopes track oxidative weathering of U minerals in Archean sediments		
15.30-16.00	Coffee Break		
16.00-17.00	Poster Session		
18.00	Reception at the GeoMuseum, Goldschmidtstraße 1-5 (optional)		

#### Friday, March 23rd: Ocean and atmosphere evolution II / Early Life

9.00-9.15	Jens Hopp, Heidelberg: Fluid inclusion assemblages in Archean cherts: p-T history and consequences for the preservation of palaeoatmospheric noble gases
9.15-9.30	Katharina Schier, Bremen: Non-detrital Gallium and Aluminum in Early Precambrian Marine Chemical Sediments and the Potential Use of the Ga/Al Ratio as a Geochemical Proxy for Metal Sources and Relative Fluxes to the Early Ocean
9.30-9.45	Ronny Schönberg, Tübingen: Isotopic investigations of the pre-Great Oxidation Event (GOE) geo- biological evolution (project 1) and the mode of atmospheric oxygen build-up at the GOE as a sharp or an oscillating process (project 2)
9.45-10.00	Wafa Abouchami, Mainz: Stable Cd isotope fractionation, diagnostic of early ocean biogeochemistry?
10.00-10.30	Coffee Break
10.30-11.00	Jan-Peter Duda, Göttingen (Keynote): Gaia obscura — understanding life at the break of dawn
11.00-11.15	Stefanie Gebauer, Berlin: The influence of biogeochemical cycles upon atmospheric habitability on the Early Earth
11.15-11.30	Michelle Gehringer, Kaiserslautern: Reconciling biological and geochemical perspectives on the production of oxygen on early Earth
11.30-11.45	Alexander Ruf, Unterschleissheim: Habitability Assessment of Primordial "Soups" using Modified Miller-Urey Experiments and State-of-the-Art Analytical Tools
11.45-12.00	Conclusion

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

# SPP1833 Building a Habitable Earth

POSTERS General Meeting 2018 SPP 1833 "Building a Habitable Earth" "Alte Mensa", Wilhelmsplatz 1, Göttingen

Katherine Armstrong, Bayreuth: Hydrogen partitioning between silicate melts and liquid sulfide: an early oxidation mechanism for the mantle

Ingrid Blanchard, Bayreuth: Behaviour of sulfur during Earth differentiation

Ludmila Carone, Heidelberg: The Archaean Earth - Coupling between geodynamics and 3D climate modelling

Annika Dziggel, Aachen: Processes of Neoarchean terrane accretion in the Nuuk region, SW Greenland

Dennis Harries, Jena: Understanding the origin of terrestrial hydrogen and carbon: metamorphism and fluids within planetesimals of the inner Solar System – Earth's nearest building blocks

Eric Hasenstab, Köln: Hafnium and Nd isotope systematics of Pilbara basalts and komatiites: changes of Archean mantle composition through time.

Achim Herrmann, Kaiserslautern: Could cyanobacteria have made the salinity transition during the late Archean?

Simon Hohl, Nanjing: Cd isotopes record changes in biologic productivity of Mesoproterozoic stromatolites

Peter Hoppe, Mainz: Iron-60 as a heat source for melting and differentiation of Earth-forming planetesimals & planetary embryos

Janos Kodolanyi, Mainz: In situ measurement of the Si isotope composition of metal and enstatite in reduced meteorites as a tracer for condensation processes and planetary differentiation during the early history of the Solar System

Inga Köhler, Jena: 3.2 Ga old microfossils in Moodies Group crinklies from the Barberton Greenstone Belt, South Africa

Florian Kurzweil, Köln: Stable tungsten isotope compositions of Earth's oldest rocks

Arne Leider, Jena: Tracing the development of early Earth's biosphere by systematic characterization of kerogens preserved in the Archean rock record

Jan Leitner, Mainz: Isotopic, chemical and mineralogical characterization of organic and inorganic nitrogen-carriers in chondritic meteorites

Christian S. Marien, Köln: 3.35 Ga carbonate interstitials from the Pilbara terrane, Australia, indicate unradiogenic 87Sr/86Sr isotope composition for the Archean seawater

Raul Martinez, Bremen: The rise and fall of archean atmospheric oxygen: did temporary carbon burial as Fe(Ox) -DOM conplexes play a modulating role?

Wladimir Neumann, Berlin: Modelling of accretion and differentiation of Earth's building blocks: Ice-rich precursors and their retention of water

Lena Noack, Berlin: Global volatile cycles on early Earth

Stefan Peters, Göttingen: Constraining the composition of Earth's late stage building blocks from the earliest ultramafic rocks

Andrea Piccolo, Mainz: Plume-Lithosphere interaction during Archean

Joachim Reitner, Göttingen: Early Archean Carbon Archives

Falko Schulz, Berlin: Effects of compressibility and non-linear rheology on the early dynamics of the solid mantle

Sebastian Viehmann, Wien: Biogeochemical reconstruction of microbial habitats during stromatolite formation using REE and Cd isotopes

Christian Vollmer, Münster: The role of ammonia for biomolecule synthesis on meteorite parent bodies

Matthias Willbold, Göttingen: Early Earth mantle heterogeneities - an isotope perspective

Jie Yao, Bayreuth: Towards melting relations in the MgSiO3-FeO+SiO2 system at lower mantle conditions from multi-anvil experiments



### Map of Göttingen and the conference locations

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

#### Stable Cd isotope fractionation, diagnostic of early ocean biogeochemistry?

Wafa Abouchami\*, Vincent Busigny, Pascal Philippot, Klaus Mezger, Harald Strauss, Chen Cheng, Stephen J.G. Galer \*Institut de Physique du Globe de Paris, 1 rue Jussieu, 75005 Paris, France wafa.abouchami@gmx.de

A large body of seawater cadmium (Cd) isotope data has become available through the concerted efforts of the international GEOTRACES program and has revealed insightful information on the biogeochemical cycling of this micronutrient in the modern oceans. In particular, the evidence that stable Cd isotope fractionation is mainly driven by biological uptake of light Cd in surface waters has led to the suggestion that Cd isotopes could potentially be a useful tracer of marine productivity. A few geological records of stable Cd isotopes have emerged suggesting that such information might be retrievable [1, 2, 3]. We will present a stable Cd isotope record of banded iron formations from various geological provinces and of different ages used as archives of past changes in ocean nutrient cycling. From the point of view of our current understanding of the modern oceanic cycle of Cd, this record indicates that the processes regulating the past cycling of Cd might have been more complex, challenging the simple use of Cd isotope fractionation as a signature of ancient bioproductivity, particularly during the Precambrian when oxygen and nutrient levels as well as ecosystems differed considerably. We will examine how the record of Cd isotope changes relates to the evolution of the ocean-atmosphere-biosphere, in response to variations in atmospheric oxygen level (e.g. NOE and GOE) and major glaciations throughout Earth's history, and draw upon the significance of Cd isotope signatures as diagnostic of paleo-productivity versus past redox state of the oceans.

[1] Abouchami et al. (2011) Goldschmidt abs., Prague.

[2] Hohl et al. (2016) GPL 3, doi: 10.7185/geochemlet.1704.

[3] John et al. (2017) Palaeogeography, Palaeoclimatology, Palaeoecology, 466, 202–208.

### High-precision measurement of $\delta^{17}$ O and $\delta^{18}$ O in carbonates by high-resolution gas source mass spectrometry – analytical setup and application

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The isotopic composition and temperature of Archean oceans is a matter of controversial debate. Archean carbonates and cherts have systematically lower  $\delta^{18}$ O values compared to their Phanerozoic counterparts [1, and references therein]. It is an ongoing debate whether this observation reflects (i) higher temperatures of Archean oceans [e.g. 2], (ii) lower  $\delta^{18}$ O composition of Archean oceans [e.g. 3], or (iii) diagenetic overprint involving isotopic exchange at high temperatures and/or with low- $\delta^{18}$ O meteoric waters [e.g. 4]. In our new approach, we aim to use the  $\delta^{17}$ O and  $\delta^{18}$ O of carbonates as *quasi* single-phase thermometer. The analytical precision required for our approach is  $\leq 10$  ppm (1 $\sigma$  SD) on the  $\Delta^{17}$ O of carbonates. Our approach provides information on both, the isotope composition of the water the carbonates last equilibrated with and the temperature of the last equilibration step. In our approach, carbonate CO<sub>2</sub> is released by conventional phosphoric acid digestion and introduced into the source of the mass spectrometer. The electron bombardment leads to fragmentation of CO<sub>2</sub> into CO and O. The  $\delta^{17}$ O and  $\delta^{18}$ O is then measured on <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O of sample and reference CO<sub>2</sub>. The high-resolution gas source mass spectrometer allows to resolve <sup>17</sup>O from <sup>16</sup>O<sup>1</sup>H and <sup>18</sup>O and <sup>14</sup>L<sup>216</sup>O, respectively. We will present the concept and the method. The method will be compared to alternative analytical protocols for the measurement of <sup>17</sup>O in carbonates and first data will be presented.

- [1] Jaffrés, J.B.D. et al. (2007) Earth Sci Rev 83, 82–122.
- [2] Robert, F. & Chaussidon, M. (2006) Nature 54, 349–392.
- [3] Shields, G.A. & Kasting, J.F. (2007) Nature 443, 969–972.
- [4] Blake, R.E. et al. (2010) Nature 464, 1029–1032.

**Hydrogen partitioning between silicate melts and liquid sulfide: an early oxidation mechanism for the mantle** Armstrong\*, K.; Condamine, P.; Abeykoon, S.; Bureau, H.; Frost, D.J. \*Bayerisches Geoinstitut, Universität Bayreuth, Universität Str. 30, Bayreuth, Germany Armstrong.Katherine@uni-bayreuth.de

After core formation, during which the presence of metallic iron in the mantle would have imposed an oxygen fugacity below the iron-wüstite buffer, the oxidation state of the Earth's mantle increased by up to 5 orders of magnitute. The timing and process(es) that oxidised the mantle have implications for the proportion and distribution of volatile elements accreted and retained within the Earth, as well as the composition of the earliest atmosphere. It is possible that the accretion of H<sub>2</sub>O-rich material led to the gradual oxidation of the mantle whilst core formation was ongoing, though only if this process could have continued once the oxygen fugacity had risen above the level where metallic iron would be stable. This implies the core-forming material would have been an FeS melt, and the oxidation reaction would then have been essentially FeS + H<sub>2</sub>O = H<sub>2</sub>S + FeO. The problem with this scenario, however, is that the resulting H<sub>2</sub>S would have to be removed from the mantle in a way that would prevent it from being oxidised and thus reversing the above reaction. In order to determine the importance of this oxidation process we have determined the partitioning behaviour of H between coexisiting silicate and sulfide melts. FeS and a MORB-composition silicate with variable Fe and FeO contents respectively were equilibrated at 3 GPa and superliquidus temperatures in a multianvil press at the BGI. Recovered samples were polished, and major elements in the silicate glass and quenched sulfide melt were determined with electron probe microanalysis. H contents of both phases were determined by elastic recoil detection analyses at the nuclear microprobe at CEA Saclay.  $D_H$ (sulfide/silicate) was found to be 0.23 ± 0.11, with little variability as a function of sulfur content in the silicate (a proxy for fO2). This implies that interaction between H<sub>2</sub>O and sulphide could have led to mantle oxidation, with the resulting H dissolving in the sulphide and being removed to the core.

#### Non-redox stable Cr isotopic fractionation of Cr(III) complexes

Babechuk, M.G., Albut, G., Kleinhanns, I.C., Wille, M., Schoenberg, R.\* \*Institut für Geowissenschaften, Musterstraße 12, D-12345 Musterstadt, Germany schoenberg@ifg.uni-tuebingen.de

The stable Cr isotope fractionation preserved in natural substances has been attributed predominantly to Cr(III)-Cr(VI) redox transformations [1]. As such, heavy stable Cr isotopic signatures in up to 2.95 billion year old iron formation have been interpreted to provide evidence for oxygenic Cr weathering of the continents and thus the existence of small amounts of free atmospheric oxygen [2, 3] up to 600 million years before the first significant rise of atmospheric oxygen levels at the so-called Great Oxidation Event (GOE) ~2.4 billion years ago. However, despite the promise that stable Cr isotopes hold as a sensitive tracer to detect redox changes at Earth's surface, the model makes several assumptions about fractionation pathways that still remain poorly constrained experimentally. Moreover, recent empirical studies have documented Cr mobility and stable Cr isotopic signatures that appear inconsistent with a simple redox driven Cr cycle. One of the most important steps forward is to carefully explore isotopic effects associated with non-redox reaction pathways (e.g., ligand-promoted dissolution, ligand exchange, adsorption of Cr(III), given that soluble Cr(III)-ligands have been directly documented or modeled in several marine, continental, and hydrothermal environments. If some of these pathways are plausible in Archean environments, they would need to be considered as an alternative or at least as a contribution to some empirical signatures. Here we report on significant inter-species stable Cr isotopic fractionation accompanying the continuous hydrolysis of Cr(III)-chloride  $[CrCl_3(H_2O)_3]^0$  via  $[CrCl_2(H_2O)_4]^{1+}$  and  $[CrCl(H_2O)_5]^{2+}$  to hexaaquachromium [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. Furthermore, preliminary experiments of Cr(III) adsorption on iron minerals revealed significant equilibrium stable Cr isotope fractionation. The stable Cr isotope variations in weathering profiles and Precambrian paleosols and iron formations will be discussed in the light of our new findings. These data should help guide the use of combined geochemical proxy information (e.g., U-Cr-Fe-Mo) in ancient Earth surface environments to better dissect the local vs. global preservation of oxygenation signatures.

- [1] Ellis, A.S. et al., (2002), Science 295, 2060-2062.
- [2] Frei, R. et al. (2009) Nature 461, 250-254.
- [3] Crowe, S. et al. (2013) Nature 501; 535-539.

#### Insight into Archean thermal evolution using P-T-t history of mafic granulites from Coorg, India

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The Coorg Massif (CM) in S. India records thermal events from ~ 3.0 Ga and consists of multiple lithologies such as charnockites, metapelites, mafic granulites and intrusive bodies of syenogranites. It is welded to the Dharwar Craton in the east and Southern Granulite Terrane in the south by a set of two Neoproterozoic shear zones. Mafic granulites from the northern boundary of CM, whether or not intruded by melts, act as indicators of lower crustal processes during the late Archean period when silicification of early mafic continental crust is thought to have occurred. A detailed petrographical study in combination with geothermobarometry and diffusion chronometry of one such sample has revealed 3 distinct metamorphic episodes based on the mineral assemblages preserved, which are as follows: (1) Initial heating of the prograde assemblage of Hbl0+Qz0 (preserved as inclusions within the garnet porphyroblast) to ~800 °C leading to the formation of Opx1, Cpx1, and Pl1 by the reaction of Hbl0 + Qz0 = Opx1 + Cpx1 + Pl1 + L or V (2) Formation of Grt, Cpx2 and Qz by the reaction of **Opx1 + Cpx1 + Pl1 = Grt1 + Cpx2 + Qz** at slightly lower temperature of ~750 °C but higher pressure of ~10.5kbar (3) Fluid influx and low T breakdown of the earlier anhydrous phases marks the final stage of evolution. During this stage, (a) retrogressed amphiboles were formed, and (b) an overgrowth of more calcic Grt2 on Grt1 with numerous quartz inclusions was formed. Possible reactions are: either Grt1 + Cpx2 + quartz + H2O = PI + Amp or Grt1 + Pl1 + quartz + H2O = Grt2 + Pl2 + Amp. Here, the "quartz" may correspond to silica from high P-T fluids. 1D diffusion modelling of preserved compositional zonations measured between Grt and Cpx suggests that these processes occurred over an extended period of time (cooling rate: 1's-10's °C/Myr) as opposed to durations of events in present day collisional settings. Our planned systematic comparison of such data with geodynamic models from present day and Archean settings will help to establish more details of the differences in thermal evolution between these periods of time in the history of the Earth.

#### Accessory minerals as archives of undisturbed primary signatures

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The formation of the first persistent crust and the availability of specific chemical components including liquid water are important key parameters for the onset of life on Earth. However, the processes that shaped the early Earth are not well understood owing to the scarcity of well-preserved Archean samples. Although rocks with ages up to 4 Ga exist on all continents, they have typically been deformed, metamorphosed, and metasomatically overprinted several times as a result of the active tectonic history of the planet. Thereby, primary mineralogical assemblages have been altered and recrystallized, and geochemical and isotopic signatures were disturbed to various extents on the sample- or outcropscale. Despite these profound elemental and mineralogical redistributions, the accessory mineral zircon has been preserved as detrital grains or xenocrysts in Archean metasediments and gneisses and represents a versatile archive: Some crystals even date back to the Hadean and provide evidence of silicate differentiation and the existence of a hydrosphere. Zircon can, however, also be susceptible to alteration, especially if it has become metamict as a consequence of radiation damage. Overall, our knowledge of the early Earth is biased by the preservation of specific sample components. The major aim of the proposed study is therefore to explore a larger variety of mineral archives in Archean rocks. Sample suites that will be investigated are: metasediments from the Narryer Gneiss Complex, Western Australia, remnants of >3.8 Ga mantle peridotites from Isua, Southern Greenland, and orthogneisses from the Acasta Gneiss Complex, Northern Canada. The minerals of interest are potentially robust accessories that are often employed in provenance studies, such as oxides (rutile, ilmenite, chromite), silicates (titanite, garnet, tourmaline), phosphates (apatite, monazite, xenotime), and sulphides. The main objectives are 1) to identify fresh, unaltered mineral grains that potentially carry primary information despite the effects of secondary alteration, and 2) to discover mineral phases that may have acted as robust 'containers' and effectively shielded their inclusions from the surrounding environment. Once identified, these time capsules will be used to determine the geochemical parameters they have preserved. In addition to major and trace element analyses, the isotope composition of Hf and Nd will be investigated to trace silicate differentiation. The results of this study will provide new insights into the history of the early Earth and facilitate more comprehensive views of its ambient environment.

#### A three component model for the refractory and volatile element inventory of carbonaceous chondrites

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The elemental composition of chondritic meteorites provides insight into the composition and the processes leading to elemental fractionation within protoplanetary reservoirs. Yet, for many trace elements, and in particular for many volatile elements the composition of chondrites is not well constrained. Here we present compositional data for carbonaceous chondrites with an emphasis on the origin of the volatile element depletion pattern. A total of 51 major and trace elements were analyzed by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS), using chondritematched calibration solutions. In general, moderately volatile elements with 50% condensation temperatures (Tc) between 1250 K and ~800 K show a monotonous depletion, while 11 moderately volatile elements with 50% T<sub>c</sub> between ~800 K and 500 K are unfractionated from each other. They are typically depleted to different degrees for different chondrite groups. Because of this well-defined pattern, we divide the moderately volatile elements into two subgroups, the 'slope volatile elements' and the unfractionated 'plateau volatile elements' with lower 50% T<sub>c</sub>. The abundances of plateau volatile elements exhibit a covariation with the matrix abundances of the respective host meteorites. Carbonaceous chondrite matrices are thus, likely mixes of two components [1]: (i) a CI-like component and a (ii) matrix component that is depleted in volatile elements and formed contemporaneously with chondrules, leading to chondrulematrix complementarity [2]. The addition of a CI-like component after chondrule formation changed the composition of bulk matrix and bulk chondrite, but refractory and main component element ratios such as Mg/Si remained CI-chondritic. In this model, the chondrule/matrix complementarity previously observed for main group and refractory elements would not be in conflict with models where chondrules and a CI-like matrix component derive from different reservoirs in the protoplanetary disk.

Jacquet, E. et al. (2016) GCA 51, 851-869.
 Hezel, D.C. & Palme, H. (2010) EPSL 294, 85-93.

Triple oxygen isotope study of a Mesoarchean Banded Iron Formation, Pongola Supergroup, South Africa Breedveld, G., Sengupta\*, S., Pack, A., M., Bau

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The temperature and the isotope composition of the Archean oceans is matter of debate. Decreasing  $\delta^{18}$ O of chemical sediments over time suggests that the Archean oceans were either very hot [1] or the  $\delta^{18}$ O of seawater was very low [2] or that the sediments themselves are diagenetically altered [3]. Banded iron formations can house information about ancient seawater. We performed petrographical and geochemical studies on the iron rich and silica rich layers of a Mesoarchean Banded Iron Formation (BIF) from the Pongola Supergroup, South Africa. The triple oxygen isotope compositions of the pure iron oxide and pure silica end members were extrapolated on basis of the Fe and Si concentrations to  $\delta'^{18}$ O<sup>quartz</sup> = 16.0 ± 1.6 ‰ and  $\Delta'^{17}$ O<sup>quartz</sup> = -102 ± 11 ppm and  $\delta'^{18}$ O<sup>iron oxide</sup> = -11 ± 6 ‰,  $\Delta'^{17}$ O<sup>iron oxide</sup> = -22 ± 23 ppm (using a reference line with slope 0.5305). The silica end member has a composition that is identical to Archean cherts from various localities, whereas composition and compositional variability of the Fe oxide layers reflects post-depositional alteration. This is also indicated by the chemical composition of the Fe oxide layers. Our data also show that the silica and Fe oxide endmembers cannot have been (at any temperature and  $\delta^{18}$ O of the water) been in equilibrium. The composition of the silica likely reflects the composition of the water the silica precipitated from early in the history of the BIF, whereas the isotope composition of the Fe oxide information on the temperatures and water composition during diagenetic alteration of these BIFs.

[1] Knauth and Epstein (1976) GCA 40, 1095–1108.

[2] Perry (1967) EPSL 3, 62–66.

[3] Degens and Epstein (1962) Bull. Am. Assoc. Petrol. Geo. 46, 534-542.

#### Uranium isotopes track oxidative weathering of U minerals in Archean sediments

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The invention of oxygen photosynthesis was a key moment in Earth history, initiating major changes in the evolution of the oceans, atmosphere and life. An increasing number of studies, based on biomarkers and the enrichment and isotope composition of redox sensitive elements, provide evidence that enhanced oxygen levels existed already before the Paleoproterozoic Great Oxidation Event (GOE), likely generated by oxygen photosynthesis. However, the onset of photosynthetic oxygenation, as well as spatial and temporal oxygen fluctuations are highly debated. Here, we present U isotope data from black shales, carbonates and iron rich sediments that were deposited from Mesoarchean to Paleoproterozoic. The analysed samples are mainly drill core samples from the Barberton- (3.23 to 3.15 Ga) and Transvaal supergroups (Ghaap and Chuniesport groups 2.588 to 2.521 Ga, Pretoria group 2.420 to 2.255 Ga) in South Africa. Subrecent U mobilisation was monitored by simultaneous analyses of  $\delta^{234}$ U and detrital contribution was monitored with Th/U. The samples show variations in authigentic  $\delta^{238}$ U from -0.83 to 0.05 ‰, significantly offset from typical  $\delta^{238}$ U of the continental crust (-0.2 to -0.4 ‰). Remarkably, we observed a significant increase in  $\delta^{238}$ U variability, with predominantly low  $\delta^{238}$ U at ~ 2.46-2.48 Ga, between samples deposited in the Ghaap group and those deposited in the Duitsland formation (Pretoria group). The light U isotope composition of the latter samples may be best explained by the onset of partial weathering of uranite, with predominantly oxidative mobilisation of <sup>235</sup>U, before the GOE. The predominantly low  $\delta^{238}$ U disappear in the overlying Timeball Hill Formation, i.e. after the GOE, which may indicate the onset of quantitative uranite weathering. In the second funding period of the SPP, we want to assess whether stromatolites may serve as archive for metal isotopic signatures (with a focus on U) by comparing modern and Proterozoic/Archean stromatolites, which experienced different kind of diagenetic overprint. We will also include microanalytical techniques. Ideally, oxic parts of stromatolites may serve as seawater archive while anoxic parts may trace microbial U reduction.

#### The Archaean Earth - Coupling between geodynamics and 3D climate modelling

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The Archaean era is an eon that brought with it great transitions in the development of the habitable Earth. The atmosphere changed drastically from an atmosphere with (likely) many times the amount of greenhouse gases today to an atmosphere with roughly present day level of CO2 and an accumulation of free oxygen. 3D climate models already proved their potential to solve the 'faint young Sun' paradox: 3D models showed that local surface water can survive with a moderate increase of greenhouse gases (10-30 present atmospheric levels of CO2), even though the Sun emitted 20% less energy during the Archaean compared to today. The presence of liquid water and moderate levels of greenhouse gases are based on various geological records but were not explainable with 1D atmosphere models. The outcome of 3D climate models, however, depends on atmosphere composition (CO2 and CH4 content), surface pressure, land/water fraction or the amount of continental crust, source and sink terms for greenhouse gases that depend e.g. on plate tectonics evolution. Many of these parameters are set for current 3D Archaean climate models as fixed initial conditions. In this project, we propose to perform a more coherent approach. Not only coupling geodynamics and climate models but also incorporating parameter constraints provided by the geological record: a series of evolution snapshots between 3.8 - 2.5 Gyrs ago with a 3D climate model in conjunction with full Archaean modelling with a state of the art 2D geodynamical model (provided by the Co-PI L. Noack) coupled to a 1D atmosphere model that will at critical times communicate with the 3D climate model to provide land mass and atmosphere composition and get albedo, ice coverage and surface temperatures to perform 1D atmo-2D geodynamics simulation between 3D snapshots. a) The geodynamics model will provide self-consistent constraints on atmosphere composition (via volcanic activity, plate tectonics and surface weathering), crustal evolution and thus land/mass fraction. b) The geological processes and Archaean atmosphere state will be bechmarked with the newest geological data that will be provided by partners within the SPP e.g. sulphur isotopes of Archaean rocks for crustal evolution (Hoffmann, Chakraborty), 40 Argon isotopes for volatile outgassing (Trieloff, Hopp) c) This project will identify critical times of plate tectonics and crustal evolution and how they will change the atmosphere gas content, surface pressures and temperatures and how these can be constrained by the geological record.

#### Light elements oxygen and nitrogen in the core of the habitable Earth

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The Earth's core is composed of iron and nickel alloyed with lighter elements, such as O, Si, S, C, H or N. It is believed that the chemical composition of the core was set during its differentiation at the base of a primitive magma ocean. Based on the Earth's elemental volatility trend relative to chondritic material, the amount of volatile light elements (particularly S, C or H) incorporated into the Earth's core is expected to be limited. Modern models of core-mantle separation, built on experimental determinations of the partitioning of siderophile elements between silicate melts and liquid metals, suggest that O and Si are potential major light element candidates. According to these models, the amount of volatile elements in the core should be below 5 at%, and for O and/or Si could be on the order of 10 at%. However, the actual abundance of volatile elements in the core could be significantly higher than these estimates, if the Earth were accreted from differentiated volatile-bearing bodies and/or if non-equilibrium processes dominated during core formation. The objectives of the first funding period were to develop a methodology for studying structures and elastic properties of iron-based alloys in situ at high pressures and high temperatures (preferably employing single-crystal based technologies), to test protocols by investigating compounds of interest in a moderate pressure range (i.e. up to 70-80 GPa), and to apply these to binary Fe-L (L=Si, O, C) systems. One of the major aims of this project is the experimental in situ investigation of phase relations in the binary and ternary systems Fe-Ni-O and Fe-Ni-N using single-crystal X-ray diffraction in laser heated DACs and studies of electronic and thermoelastic properties of the phases. We will obtain information crucial for understanding the processes related to the chemical differentiation of the Earth to contain a metal core, for modeling the past and present history of the core, and for understanding the effect of core formation on the development of a habitable planet.

Modelling the origin of Earth's water within constraints by noble gas isotope systematic Dullemond\*, C., Trieloff, M. \* Universität Heidelberg, Zentrum für Astronomie (ZAH), Institut für Theoretische Astrophysik (ITA), Albert-Ueberle-Str. 2, 69120 Heidelberg dullemond@uni-heidelberg.de

Water is one of the most important ingredients that make the Earth a habitable planet and was present over most of its history. It is generally assumed that Earth acquired a certain fraction of outer solar system planetesimals bringing water to Earth. The cometary or asteroidal origin of terrestrial water is conventionally traced by comparing hydrogen isotopic composition of Earth, meteorites and in situ or remote measurements of comets. However, this approach leads to inconclusive results. We envisage a fundamentally different approach: Combining astrophysical modeling of early planetary accretion, and cosmochemical and geochemical studies of noble gases - He, Ne, Ar, Kr and Xe - as tracers of the origin of the atmosphere and hydrosphere. In this way we address previously neglected or unrecognized mechanisms that could provide water to the accreting Earth from the very beginning, instead of just as a "late veneer".

#### Processes of Neoarchean terrane accretion in the Nuuk region, SW Greenland.

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The geodynamic processes by which the Archean crust was created and reworked are a matter of intense scientific debate, and both plate tectonic and vertical tectonic models have been proposed. For many Archean provinces, it is plausible that some of the steep shear zones commonly interpreted as terrane boundaries originated from partial convective overturn of gravitationally unstable crust. Nevertheless, some Archean orogens, e.g. in the Nuuk region in SW Greenland strongly resemble younger orogenic systems in that they preserve evidence for regional-scale crustal thickening and the existence of distinct terranes characterized by different thermal regimes and PT histories. In the Nuuk region, crustal convergence resulted in the collision of the Færingehavn terrane with the structurally overlying Tre Brødre and Tasiusarsuaq terranes [1]. In the Tasiusarsuaq terrane, nappes of deep crustal granulites (800-950°C, 9-12 kbar) were exhumed into mid crustal levels during NW-vergent thrusting at ca. 2.76-2.72 Ga, coeval with underthrusting of the Færingehavn terrane [2]. 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. The deep crustal granulites are thus interpreted to represent hot, ductile fold nappes such as those suggested for large hot orogens [2]. For the second funding period, we plan to test two contrasting hypotheses (terrane accretion versus later reworking of a once continuous segment of Archean crust) for the formation of the Lewisian Complex, Scotland, using a combination of phase diagram modelling and in situ U-Pb, Lu-Hf, O isotope and trace element analysis of zircon. The main aim of this study is to provide a better understanding on the timing and conditions of crust formation and reworking, and to clarify if the crustal blocks are indeed terranes or if they represent different crustal levels of a once continuous Archean continent.

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[2] Dziggel, A. et al. (2017) Prec.Res. 300, 223–245.

#### Ruthenium isotope constraints on the timing of volatile element accretion

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The Earth formed by accretion of numerous planetesimals and planetary embryos originating from various heliocentric distances. Depending on the location of their formation region these planetary building blocks are characterized by different contents of water and volatiles with the highest volatile abundances expected in objects formed at greater heliocentric distance [1]. While it is largely accepted that water and other volatiles were brought to the Earth by the accretion of carbonaceous chondrite-like materials originating from the outer solar system [2,3], the timing for the accretion of these volatile-rich objects has been the subject of significant debate [4-6]. Some of these models propose that water and volatiles were added to the Earth during late accretion of a late veneer after core formation had ceased [4-7]. However, the accretion of the Earth's volatiles as part of the late veneer cannot be reconciled with recently reported Ru isotopic data for primitive meteorites [8], which show that the late veneer cannot be comprised of volatilerich carbonaceous chondrite-like asteroids. This is because 1.) the Ru in the Earth's mantle almost exclusively derives from the late veneer, and 2.) carbonaceous meteorites on average display the most distinct Ru isotopic composition compared to the terrestrial mantle. The major implication from this result is that Earth must have accreted its budget of volatile elements during earlier stages of accretion [8]. Hence, finding a genetic signature unique to carbonaceous chondrite-like material and investigating its presence in the Earth's earliest geological record is key to unravel the timing of volatile element accretion. Mass-independent Ru isotopic variations among cosmochemical materials have been shown to be powerful genetic tracers for volatile-rich material. This is because volatile-rich carbonaceous chondrites exhibit distinct Ru isotopic compositions compared to the volatile-poor meteorites [8,9]. In case of Ru these signatures were most likely preserved only in the early Archean mantle before it was overprinted by the late veneer and homogenized due to mantle convection. The goal of this study is to assess whether the Archean mantle contains isotopic signatures imparted by the accretion of volatile-rich carbonaceous chondrite material. To address this, we are currently investigating the Ru isotope composition of chromitites from different Archean mantle domains in South Africa (Barberton), Pilbara (Australia), Seqi and Itsaq (Greenland).

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- [7] Wang, Z. & Becker, H. (2013) Nature 499, 328-331.
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### The behaviour of Sn and In during mantle melting and fractional crystallization: Implications for moderately volatile abundances in Earth's interior.

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Part of what makes Earth unique and able to sustain life is its distinctive "cocktail" of chemical elements. Of these, the moderately volatile elements (MVE), which include elements like Sn, In, Sb, Ag, Ge, Ga, Bi, and As, are among the most challenging to characterize with their behaviour during the formation of the Earth. Despite their clear importance, it is surprising that MVE behaviour in high temperature systems is poorly understood. In particular, there is a debate on how the concentrations for the MVE were added to the bulk silicate Earth (BSE). Competing processes, like core formation, volatile loss, and, potentially, late volatile addition, may have contributed to the present-day abundances of these elements in BSE. Part of the problem is that there is a great deal of uncertainty on how to estimate MVE abundances in BSE. There are few experimental studies aiming to understand how the MVE behave during partial melting of the mantle. Indeed, most of the data available in the literature pertain to the behaviour of first row transition elements like Ni, Cu, Zn, and Pb; yet there is a scarcity of partitioning data for elements like Sn, In, and Sb, for example. Moreover, MVE abundances in basalts and mantle samples (i.e. peridotite xenoliths) are difficult to obtain due to analytical limitations. Also, it is yet unknown to what extent magma chamber processes, like tapping, crystallization and replenishment may affect the MVE abundances record in basalts.

Here we present new experimental data pertaining to the partitioning behaviour of Sn, In and other MVE during mantle melting and crystallization, as well as to the oxidation state of redox sensitive MVE like Sn. We find that while Sn and In are relatively compatible during partial melting of Earth's mantle when compared to lithophile elements like Sm and Y, they are highly incompatible at the lower pressure conditions that preside over fractional crystallization and tapping of magma chambers. This phenomenon is related to the presence of Ca-Tschermark component in mantle clinopyroxene, which is less important during fractional crystallization, which raises Sn and In mineral/melt partition coefficients. Our results indicate that the behaviour of Sn and In, as recorded by basalts is not directly relevant to their behaviour during melt extraction from a mantle source. This view is reinforced by recently obtained high-precision isotope dilution Sn-In concentrations, which show a clear decoupling of Sn-Sm and In-Y between basalts and their mantle sources. We propose to carry out a detailed experimental campaign to fully explore the role that changing redox conditions and mineral and melt composition have on the high-temperature behaviour of the MVE during magmatic processes. These data will be used to fully understand the how the MVE are mobilized from the mantle to the crust, and ultimately provide robust constraints on the abundance of these elements in BSE.

# The influence of biogeochemical cycles upon atmospheric habitability on the Early Earth (1) The impact of improved geologically-constrained environmental data on the atmosphere and biosphere (2) The effect of co-evolving biogeochemical cycles on habitability

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This presentation consists of two sections: (1) we describe work performed during the first funding period and (2) work proposed for the second funding period.

(1) Understanding the evolution of Earth is essential to fathom our origin in the Universe. The Great Oxidation Event (GOE) denotes the first major rise of molecular oxygen (O2) in Earth's history. The timing and magnitude of the GOE was likely related to the interplay between the major reservoirs, namely the atmosphere, hydrosphere, biosphere and geosphere. As a consequence, the planet experienced the emergence of widespread habitability and complex life. The origin and controlling mechanisms of this spectacular event are still not well understood, the study of which requires interdisciplinary, coupled models. Recently there has been a revolution in improved methods for constraining geological data (for e.g. atmospheric pressure, composition, ocean temperature etc.) of the early Earth. In this study we investigate the influence of the new data upon our understanding of key processes which drove the GOE by applying our newly updated Coupled Atmospheric Biogeochemical (CAB) model [1].

(2) Biogeochemical cycles govern the release of chemical species into the atmosphere and therefore have an essential impact upon the habitability of Earth. Since these cycles are strongly coupled we plan to extend our CAB model (which currently includes the oxygen cycle) to incorporate the carbon and nitrogen cycles. We will then assess their impact on the habitability of Early Earth and the magnitude and timing of the GOE. With this new approach, surface O2 concentrations from the evolutionary pathway derived from proxy data will no longer be an input parameter but will instead represent an output parameter of the model aiming to reproduce consistently the GOE. Furthermore, in collaboration with experimental studies performed by M. Gehringer within the SPP framework, we will constrain the amount of O2 which could have been released during so-called "whiffs" of O2 into the reducing Archean atmosphere. Our approach is novel due to our consistent treatment ofbiogeochemical cycles driven by the incorporation of proxy and laboratory data. We evaluate thereby theextent by which the relevant theory is consistent with biological/ geological data and implement improvements where needed.

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#### Reconciling biological and geochemical perspectives on the production of oxygen on early Earth.

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The Great Oxygenation Event (GOE) is the period during which the level of free O<sub>2</sub> in the Earth's atmosphere rose from zero to above ~ 10<sup>-5</sup> times that of today. However, evidence of early pockets of localised oxygenation, the so called "whiffs", are being found in Archaeal shallow water environments and subaerial crust. When considered together with recent genomic phylogenetic investigations indicating that cyanobacteria, the only bacteria able to conduct oxidative photosynthesis, arose at least 2.7 Ga, and that the oxidative splitting of water evolved even earlier, the question arises as to why it took another 0.3 Ga for the oxygenation of the Earth's atmosphere. One hypothesis is that limitation of bioessential nutrients such as nitrates, phosphates and trace metals, meant that the cyanobacteria were unable to thrive. Another hypothesis suggests that localised oxidation of subaerial crustal minerals adsorbed O<sub>2</sub> released by cyanobacteria. This project addresses these hypotheses by utilising liquid cultures of both marine and freshwater nitrogen fixing cyanobacteria to determine the rates of photosynthesis and biological nitrogen fixation under a reducing, anaerobic Archean atmosphere with elevated CO<sub>2</sub>. Pursuant to this are trials to assess the effects of nutrient limitation on cyanobacterial primary production during the Archean. By generating pseudomats on a solid matrix of ground rocks, we will be able to determine the exact interactions occurring at the mineral:microbe interface with respect to  $O_2$ concentrations as well as pH and Redox changes. Combining data from the individual, synchronised liquid cultures with that obtained from pseudomats, will provide insight into the growth and physiological responses of modern-day descendants of ancient cyanobacteria at the level of the individual organism AND the ecological community response in mats. The experimentally obtained data will be compared to the total N and trace element content determined for organic rich layers of preserved microbial mats and stromatolites from marine and non-marine settings. This is the first study to investigate the potential nutrient limitations on cyanobacteria during the late Archean, and their ability to source essential trace elements via weathering of their mineral substrates, leading up to the GOE.



Fig. 1: Graphical representation of Archean mineral:microbe weathering studies. Increased pH ( $\sim$  9-10) and increased O<sub>2</sub> levels have been shown for endolithic cyanobacteria grown under PAL and under reduced O<sub>2</sub> atmospheres on quartz sand. We intend to repeat these experiments under a reducing Archean atmosphere on a basalt substrate. Localised alkalisation results in deprotonation of Si-O-H bonds in silicates, leading to bioweathering of rock and the mobilisation of essential elements such as Mo and P by increased levels of O<sub>2</sub>. Increased supply of these bioessential elements would promote increased cyanobacterial growth, and hence O<sub>2</sub> production, with possible wash off of oxidised elements such as phosphates, sulphates and molybdates into local water bodies. The extracellular polymeric substances (EPS) indicated as yellow, would trap the oxygen locally (represented as red circles), thereby delaying its release into the atmosphere and allowing time for the bioweathering reactions to occur.

#### Double diffusive convection and Layer Formation in Planetary Mantles

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The thermal history of the Earth, it's chemical differentiation and also the reaction of the interior with the atmosphere is largely determined by convective processes within the Earth's mantle. A simple physical model, resembling the situation, shortly after core formation, consists of a compositional stably stratified mantle, as resulting from fractional crystallization of the magma ocean. The early mantle is subject to heating from below by the Earth's core and cooling from the top through the atmosphere. Additionally, internal heat sources will serve to power the mantle dynamics. Under such circumstances double diffusive convection will eventually lead to self organized layer formation, even without the preexisting jumps is material properties. We have conducted 2D and 3D numerical experiments in Cartesian and spherical geometry, taking into account mantle realistic values, especially a strong temperature dependent viscosity and a pressure dependent thermal expansivity. The experiments show that in a wide parameter range. distinct convective layers evolve in this scenario. The layering strongly controls the heat loss from the core and decouples the dynamics in the lower mantle from the upper part. With time, individual layers grow on the expense of others and merging of layers does occur. We observe several events of intermittent breakdown of individual layers. Altogether an evolution emerges, characterized by continuous but also spontaneous changes in the mantle structure, ranging from stagnation of slabs at various depth to variations in the chemical signature of mantle upwellings in a new framework.

### Understanding the origin of terrestrial hydrogen and carbon: metamorphism and fluids within planetesimals of the inner Solar System – Earth's nearest building blocks

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The origin of Earth's water and carbon has not been resolved compellingly. The late delivery of Earth's water by typical comets has been excluded, and also hydrous, carbonaceous chondrites of the outer Solar System are under critical scrutiny due to mismatching isotopic constraints [1]. In turn, ordinary and enstatite chondrites may be remnants of a reservoir of planetesimals in the inner Solar System that contributed to the main accretion of the terrestrial planets. Particle RA-QD02-0115 returned by the Hayabusa spacecraft from the LL-chondritic near-Earth asteroid 25143 Itokawa contains sub- $\mu$ m-sized grains of the iron carbide haxonite, as well as ellipsoidal to nearly spherical voids [2]. Based on these observations, thermodynamic modelling indicates the presence of a methane-rich fluid during thermal metamorphism of Itokawa's parent body. Mass balancing of carbon (from macromolecular organics) and hydrogen (from co-accreted ice) indicates an initial ice/rock ratio of about  $7 \times 10^{-3}$  by mass in the source region of RA-QD02-0115. This suggests approx. 695 ppm initial bulk H<sub>2</sub>O in the chondritic assemblage. H<sub>2</sub>O concentrations as low as 100 ppm in Earth's early mantle could have produced a steam atmosphere and a primitive ocean upon cooling [3]. Thus, small indigenous hydrogen contents of ordinary and enstatite chondrites may have provided a significant fraction of the terrestrial water. However, the concentration of hydrogen in ordinary and enstatite chondrites and its evolution and retention during radiogenic heating of planetesimals need much better understanding in order to constrain the delivery of volatiles to the early Earth.

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### Hafnium and Nd isotope systematics of Pilbara basalts and komatiites: changes of Archean mantle composition through time.

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The composition of ancient mafic to ultramafic successions allows inferences on the depletion history of Earth's mantle. Although Hf and Nd isotope compositions have become an indispensable tool for investigating modern and palaeo mantle-curst evolution, their evolution is still highly discussed for Archean rocks [1]. For this study, 21 pristine samples from the Pilbara Craton were selected for high precision Hf and Nd isotopic composition measurements in order to better constrain the history of the Archean mantle. These sample suites studied here can roughly be divided into two volcanic associations. (1) The oldest units (Warrawoona Group, Kelly Group, Roebourne Group, Soanesville Group and Dalton Suite; 3525 - 3180 Ma) show flat to slightly LREE depleted trace element patterns that are mostly attributed to plume volcanism [2]. (2) The younger units (Whundo Group, Croydon Group and Fortescue Group; 3120 – 2772 Ma), however, show more diverse trace element patterns LREE enrichments. Especially the Whundo Group and Fortescue Group can be attributed to subduction related volcanism and large igneous province (LIP) volcanism, respectively. This is also in accord with low Nb/Th and high La/Yb<sub>CN</sub> ratios for these younger samples that indicate that the sources of these rocks were affected by an enriched lithospheric component. Because the investigated samples have preserved pristine magmatic features and major vs. trace element trends, Hf and Nd isotope data of these rocks are sufficiently robust to determine the depletion history of their mantle sources.  $\varepsilon$ Hf(t) and  $\varepsilon$ Nd(t) are both slightly superchondritic and span a narrow range that varies from 0 to +3.2 and +0.3 to +2.0, respectively. Only the youngest dikes of the Fortescue Group show a negative εHf(t) and εNd(t) value of -2.7 and -2.8, respectively. Although the samples cover a wide age range from 3525 Ma to 2775 Ma, the younger samples do not show increasingly radiogenic Hf or Nd compositions, as would be expected for an isolated depleted mantle domain. Rather,  $\varepsilon Hf(t)$  and  $\varepsilon Nd(t)$  stay constant during this period of time, as previously observed [3]. These constant  $\varepsilon Hf(t)$  and  $\varepsilon Nd(t)$  values might be explained by continuous mixing between a primitive mantle domain with a long-term depleted domain. This model can also account the persistently positive  $\varepsilon$ Hf(t) and  $\varepsilon$ Nd(t) values although plume melts should have EHf(t) and ENd(t) clustering around the chondritic value, because these melts were extracted from a primitive mantle. After the onset of plate tectonics at ca. 3120 Ma as indicated by the occurrence of island arc basalts of the Whundo Group the Hf-Nd isotope signatures might alternatively be explained by assimilation of a continental crust or an enriched lithospheric mantle component.

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#### Tidal heating in the early Earth-Moon system under a faint, young sun

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Geological samples, whether terrestrial or extraterrestrial, currently serve as the principal vestige into the Archean age. We propose to employ a novel approach in which we combine existing measurements of the ongoing orbital recession of the Earth's Moon with early evidence of tidally-affected sedimentary patterns to test new numerical simulations of the early Earth-Moon system. Our aim is to study the orbital evolution of the system to explore the contribution of tidal heating to the energy budget of the young Earth. The main goal is to solve the riddle of the early presence of liquid surface water on Earth, at a time when the Sun's luminosity was too small to generate sufficient surface heating to prevent a global snowball. We have previously performed similar studies in the context of Earth-like extrasolar planets, that is, planets beyond the solar system [1,2]. A few dozens of these Earth-sized exoplanets have been found over the past few years and it has now become possible to characterize their orbits as well as the illumination received from the star. We have developed a numerical model to simulate the energy flux of such Earth-like planets during their evolution under the effects of an evolving star and an evolving planetary orbit. We found that the first few 100 million years are critical for an Earth-like planet to either sustain significant amounts of liquid surface water or lose it all through a runaway greenhouse effect. This process is crucial for the habitability of an Earth-like planet, see Venus which has become desiccated through a runaway greenhouse effect due to enhanced solar illumination although this planet is otherwise Earth-like in many regards. In the context of the SPP 1833, we want to explore the combined effects of tidal heating in the early Earth, which was generated when the Moon was much closer than it is today, and of the evolution of the solar flux, the latter of which was only half of what it is today. We suggest that the consideration of tidal heating has the potential to solve the longstanding faint young sun paradox. The ultimate question that we strive to answer is "How to build a habitable Earth under a faint sun?".

[1] Heller, R. et al. (2011) A&A 528, A27, pre-print:https://arxiv.org/abs/1101.2156.
[2] Heller, R. et al. (2018) in preparation.



Figure: Evolution of the energy flux on an Earth-like planet during the first 1000 million years of its evolution. The total energy flux is shown with a black, solid line. It is composed of the absorbed stellar illumination (blue, solid line) and the geothermal flux (red, dashed line), the latter of which is dominated by tidal heating in our simulations. We do not consider the effects of a moon in this particular model but rather assume that the orbit of the planet around its star is eccentric, which causes the tidal friction and the resulting heating in the planet. These are preliminary results from an ongoing collaboration of the investigators on this proposal [2].

#### Could cyanobacteria have made the salinity transition during the late Archean?

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Modern molecular evolutionary studies suggest the freshwater origin of cyanobacteria during the late Archean, about 2.7 Ga ago, with an even earlier evolution of oxygenic photosynthesis. The large amount of oxygen required to oxygenate the Earth's atmosphere during the Great Oxygenation Event (GOE) ~2.4 Ga is thought to have been produced by large cyanobacterial blooms in the open ocean. This then poses the question as to whether ancient lineages of cyanobacteria would have survived the salinity transition. This study investigates the effect of increasing salinity on the photosynthetic efficiency of two modern day descendants of ancient cyanobacteria, Chroococidiopsis thermalis PCC7203 and the root species, Gloeobacter violaceus PCC7421. Organisms were cultured in fresh, brackish or sea water analogous media under a present atmospheric level (PAL) atmosphere or an atmosphere with reduced O2 and elevated CO2 (rO2eCO2). The gross photosynthesis (GP) rates were determined in liquid cultures, while the O2 profiles were determined in pseudomats. While C. thermalis PCC7203 was able to grow under increasing salinities under both atmospheres tested, G. violaceus PCC7421 could not make the salinity change to sea water. GP rates were reduced for C. thermalis under increasing salinities, as were the levels of dissolved O2 in the media. A gene screen indicated that C. thermalis genome carries genes for both trehalose and sucrose synthesis, whereas G. violaceus has only the later genetic component, suggesting a mechanism for their differing salt tolerances. This study supports the hypothesis of Cyanobacterial evolution in freshwater environments and their transition into increasingly salty environments during the late Archaean, prior to the GOE.

### Leveraging the record of the Swazi Barberton Greenstone Belt for an improved understanding of Archean tectonostratigraphic processes

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The Barberton Greenstone Belt (BGB) contains one of the world's very few high-quality stratigraphic archives of Archean surface conditions; its style of deformation also provides critical information on early-earth lithospheric processes and continent formation. Nevertheless, the vast majority of scientific contributions to the understanding of the BGB, of Archean deformation styles and Archean nonuniformitarian processes have come from the South African part of the BGB; its geology in Swaziland has – for various reasons – contributed little, and its publications have generally found little attention in the scientific discourse. However, some key stratigraphic units in the Swazi part of the BGB are better exposed, have a fundamentally different provenance, age, metamorphic grade and regional deformation style. None of these differences has been considered seriously in any models of the tectonostratigraphic evolution of the entire BGB to-date.

I propose to extend the focus of my past and current research projects from South Africa into Swaziland, building on legacy geologic maps and intriguing preliminary geologic, tectonic, petrographic, geochronologic and stratigraphic findings from BGB units. This will contribute to construct a consistent greenstone-wide model of its tectonic and stratigraphic evolution and help to evaluate competing models of continental growth.



**Fig.:** Left: Geologic map of part of the BGB in northernmost Swaziland. The reassignment of the lava unit (grey) to the Moodies Group will greatly facilitate the basinwide correlation of Moodies strata when correlated into South Africa. Right: View from Swaziland across the border into South Africa, illustrating outcrop quality.

### The role of early Archean Terrestrial Environments in Weathering, Sediment Transport, and the Colonization of Land Heubeck\*, C.

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Archean terrestrial strata preserve a unique and potentially valuable record that allows constraining the history of interaction between geo-, bio and atmosphere: It includes conditions of paleosol formation, 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 mechanism and degree of nutrient delivery, strategies of radiation avoidance, 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. In a wider context, constraining past processes on land (and the direct interaction of the terrestrial geosphere with the atmosphere) is important because exposed land regulates the CO<sub>2</sub> content of the atmosphere through silicate-carbonate weathering and other chemical weathering processes. It would therefore be valuable to gain at least a first-order understanding of the processes occurring on land in the deep geologic past. Although Archean terrestrial depositional systems are rare and generally poorly preserved for a number of reasons, their potential value warrants their detailed investigation.

We here suggest the investigation of the Early Archean (3.22 Ga) Moodies Group, South Africa from which the world's oldest purportedly eolian strata have been reported. Our preliminary surveys have documented microbial mats, evaporite concretions, and a sedimentary breccia unit but have to-date been unsuccessful in confirming eolian strata. Geological mapping, section measuring, textural studies, evaporite analysis and sandstone petrography will constrain the terrestrial settings, improve our understanding of Archean terrestrial processes and constrain related SPP research projects. This may even extend to conditions on Mars where aqueous environments were (and are) far more tenuous.

#### Comparison of Early Archean "sag basins" to subrecent salt basins through field work and numerical modelling

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Field structural and sedimentary mapping, combined with numerical modelling and thermochronology, shows that the earliest sedimentary basins, preserved in Archean greenstone belts, are likely products of a unique nonuniformitarian process: They originated predominantly by sagging between rising plutons and are affected by significant subvertical strain. (Sub-)horizontal strain, commonplace in post-Archean plate-tectonic settings, appears subordinate. This process is difficult to document quantitatively in the Archean due to a paucity of prime outcrop, widespread subsequent metamorphism and the comparatively small size of preserved greenstone belts. However, the process of basin formation may have a recent close geometrical analogue in salt provinces of arid climates where syndeformational basins are fed principally by clastics eroded from large nearby domes overlying vertically rising salt diapirs.

We suggest to study geometry, basin-fill architecture, drainage evolution, and provenance of selected Miocene to Recent basins in the Fars region of the Zagros Mountains of southern Iran, worldwide unique in being the only onshore laboratory conducive for this type of study. Findings from field work (basin margin geometries, intraformational unconformities, sediment dispersal vectors, rates of uplift and subsidence etc.) will be incorporated in geomorphological-thermomechanical numerical models and compared to highly deformed syndeformational Archean basins. We selected the Moodies Group (3.22 Ga) of the Barberton Greenstone Belt (BGB), South Africa, as the as the principal target but will also compare our findings with the Pilbara Supergroup (ca. 3.5-3.2 Ga) and De Grey Supergroup (3.0-2.9 Ga) of the East Pilbara Terrane of the Pilbara Craton, Australia. Our findings will test process-related hypotheses of continental crust formation, lithospheric rheology, and high depositional and deformational rates.



Fig.: Structural and strati-graphic relationships style at many greenstone belt margins (here along the northern margin of the BGB) resemble those adjacent to modern salt diapirs.

### The ICDP BASE (Barberton Archean Surface Environments) Project: Probing the Moodies Group, Barberton Greenstone Belt, South Africa

Heubeck\*, C., and the BASE Team\*\*

\*\* https://www.icdp-online.org/projects/world/africa/barberton-3-s-africa/

We report on a submitted ICDP Full Proposal with the objective to drill sedimentary strata of the Early Archean Moodies Group of the Barberton Greenstone Belt, South Africa. The sedimentary (and minor volcanic) strata of this unit (~3.22 Ga, ~3.7 km thick) were deposited within ~1-14 Ma and thus record at very high resolution Archean surface processes in conglomeratic and sandy fluvial to silty, shaly and cherty prodelta environments. Despite tight regional folding, metamorphic grade is only lower greenschist facies; widespread early-diagenetic silicification preserved abundant microand macrotextures virtually without strain. The strata allow the regional and temporal contextualization of highresolution analytical data and record numerous bio-geo-atmo-hydrosphere interactions. They are ideal to investigate Archean terrestrial-marine transitions, particularly those related to diverse and well-documented microbial life. The "earth system" and "global environmental change" topics support the themes of a nascent UNESCO world heritage site likely to be declared in the Barberton Mountain Land in 2018.

During a field workshop in October 2017, in which 48 scientists from 11 countries participated, we inspected and prioritized numerous potential sections. Four focus groups (life, paleoenvironment, "hard rock", and sedimentation dynamics) defined eight inclined drillholes of 300-600m length each, targeting transitions between thick tidal microbial mats, fluvial and coastal gypsiferous paleosols, shoreline systems, delta complexes, potentially eolian strata, and prodeltaic jaspilites and banded-iron formation.

Principal questions include the causes of stratigraphic rhythmicity, the origin of coastal BIFs, metabolism of tidal microbial mats, composition of oceans and atmosphere, origin and role of paleosols, the paleomagnetic roecord and Archean basin dynamics. A decision on ICDP funding is expected for late June 2018.

#### Elucidating Eoarchean geodynamic processes using multiple S isotopes

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The style of Archean geodynamic processes as well as the geodynamic setting of early continental crust formation are currently highly debated. Based on a well-characterized set of Eoarchean samples from the >3.7 Ga Isua Supracrustal Belt and adjacent areas in Greenland, we will investigate how crustal recycling processes operated in the early Archean. We use bulk rock and in situ multiple sulfur isotope compositions of Eoarchean oceanic crust, mantle peridotites and continental crust to trace recycling of material, which interacted with the ocean-atmosphere system, into the mantle and by melting processes into early continental crust. By performing bulk rock and in situ sulfur isotope compositions of sulfides together with petrographic observations, we test if mass-independent fractionated sulfur (MIF-S) was incorporated in hydrothermally altered oceanic crust, then transferred into the mantle and subsequently incorporated in the early continental crust that possibly sourced from thickened proto-arc crust. Thus, we place constraints on the early Archean magmatic and hydrothermal sulfur cycle and investigate, if crustal recycling processes comparable to present-day subduction were operating.

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#### Cd isotopes record changes in biologic productivity of Mesoproterozoic stromatolites

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We studied high resolution trace element abundances and stable C, O and Cd isotope compositions in carbonate leachates of stromatolites from two locals within the Mesoproterozoic Paranoa Formation, Brazil. Marine-like shale normalized REY patterns and lack of correlation between conservative (Hf, Zr, Al) and fluid-mobile (Sr, Mn, Ba) elements and O isotopes in carbonate leachates argue for a negligible syn- and postdepositional overprinting on carbonates and can be used to reconstruct the paleoe-envrionment in which the two stromatolite morphologies thrived (see Poster by S. Viehmann this meeting). Cd isotopes in carbonates are a novel proxy for studying biogeochemical conditions in paleoenvironments under the premise that Cd concentrations and isotopic compositions in modern seawater reflect nutrient utilisation of Cd by photosynthetic organisms. The overall variation in Cd isotopic compositions of the stromatolite localities studied is 7 ɛ<sup>112/110</sup>Cd units and exceeds that of crustal rocks. The Cd isotopic compositions in Sao Gabriel stromatolites are unfractionated and match that of the upper crust, indicating that dissolved terrigenous Cd was delivered via weathering and erosion of the continental hinterland into the Sao Gabriel lagoon. By contrast, the  $\epsilon^{112/110}$ Cd values in carbonate leachates from the Fazenda Funil locality show a wider spread in values plotting along a fractionation line between two carbonate endmembers with  $\alpha$  = 1.00046: Endmember I shows low  $\epsilon^{112/110}$ Cd values with high Cd and U but low Mn and Ce concentrations that was formed under oxic conditions at the seawater-microbial mat interface closely resembling ambient Late Mesoproterozoic seawater. Endmember II shows high  $\epsilon^{112/110}$ Cd values that coincide with low Cd and U and higher Mn and Ce concentrations. These carbonates formed under suboxic/manganous conditions from the ambient pore-fluids within the microbial mat. In this scenario, Mn and Ce were released from the breakdown of colloids in a semi-closed system while the Cd isotope composition in the ambient fluid was further fractionated into biomass and carbonates, leading to more positive  $\epsilon^{112/110}$ Cd values in ambient pore-fluid and carbonate via the combined effect of Rayleigh fractionation by biological Cd uptake and kinetic fractionation of Cd into carbonate minerals. Hence, we showed that Cd concentrations and isotope measurements of the oldest so far analyzed biogenic carbonates have a huge potential in the future to understand biological processes of the earliest life on Earth and potentially extraterrestrial planets and may further be used to understand carbonate formation in stromatolites and (micro)nutrient cycling in ancient microbial environments.

### Fluid inclusion assemblages in Archean cherts: *p*-*T* history and consequences for preservation of palaeoatmospheric noble gases

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Noble gas isotopes can add valuable constraints about the degassing history of the Earth's interior. A major reason for this is the continuous production of radiogenic isotopes (e.g., <sup>4</sup>He and <sup>40</sup>Ar) from long-lived decay systems (K-Ar, U-Th-He). On the other hand, some noble gas isotopes are exclusively primordial in origin (e.g., <sup>36</sup>Ar). Hence, any variation of the atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar-ratio through time is a sensitive indicator of changes in the degassing flux of the solid Earth. However, deciphering the noble gas record of the ancient atmosphere is troublesome because of a couple of issues. (1) Ancient noble gases might be not retained in their original host due to thermal or chemical processing. (2) Exchange with or superposition of modern air, which is the by far largest noble gas reservoir on Earth, may obscure any palaeoatmospheric contribution. (3) In-situ ingrowth of radiogenic isotopes with time commonly requires large corrections leading to a low precision for the isotopic compositions of interest. (4) Finally, even quite low-grade metamorphic events frequently are associated with fluid migration in the crustal section. Crustal fluids are characterized by significant additions of radiogenic isotopes and noble gases with an ambient atmospheric provenance at the time of metamorphism. Therefore, even well-preserved Archean sedimentary rocks contain several generations of fluid inclusion assemblages entrapped during various episodes. We performed a microthermometry-study of fluid inclusions in Archean cherts from South Africa (Mendon Formation) in order to reconcile their fluid entrapment history and to search for primary fluids as potential carriers of ancient atmosphere and as targets for noble gas analyses. Evidently, there are several episodes of fluid capture documented in our cherts indicating a widespread infiltration of crustal fluids during at least one low-grade metamorphic event (estimated max. T ca. 500°C). Only in case of the Buck Ridge chert a possible primary fluid inclusion assemblage was identified, which may have formed within a hydrothermal system close to the surface (max. T ca. 160°C).

#### **Iron-60 as a heat source for melting and differentiation of Earth-forming planetesimals & planetary embryos** Hoppe\*, P., Vollmer, C.

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The level at which radioactive 60Fe (half-life: 2.62 Myr) was present in the solar nebula and whether its decay could have made an important contribution (in addition to 26AI) to the melting and differentiation of planetesimals, the building blocks of the terrestrial planets, is still highly uncertain. To which extent the building blocks of the Earth were already differentiated has strong impact on how Earth's core and mantle came into its present configuration and on the abundances of volatile elements (e.g., H, C, N) and water, important components for building a habitable Earth. In view of the predicted production of 60Fe in asymptotic giant branch stars and supernovae it appears plausible that 60Fe could have been present with significant abundance in the solar nebula. The application of a combination of several nano- and microanalytical analysis techniques to meteoritic samples proposed here is aimed to put better constraints on the level of 60Fe in planetesimals that later formed the Earth. Our experimental approach relies on Fe-Ni isotope measurements with high spatial resolution and a thorough mineralogical characterization of analyzed sample spots. We will use the new oxygen primary ion source (Hyperion II from Oregon Physics), which was recently installed on the NanoSIMS ion probe at MPI for Chemistry, to conduct Fe-Ni isotope studies at much smaller scales than was possible before. Objects with high Fe/Ni ratios, a pre-requisite to identify 60Ni excesses from 60Fe decay, will be pre-selected on the basis of combined SEM-EMPA investigations of several meteorites that experienced only minimal aqueous and thermal alteration. Followup studies of identified objects with 60Ni excesses will be conducted by FIB/TEM and by RIMS (CHILI at the University of Chicago) to validate inferred 60Fe/56Fe ratios. FIB/TEM will be used to characterize the mineralogical context and to constrain the degree of disturbance of the Fe-Ni isotope system by possible secondary alteration processes and presence of nanometer- to submicrometer-sized metal and sulfide inclusions within the analyzed minerals. Iron-Ni isotope studies with CHILI will be used to verify observed 60Ni excesses to exclude potential unidentified isobaric interferences and extreme intrinsic mass fractionation effects not recognized in the preceding NanoSIMS studies.

### Investigating the roles of Fe(II)-silicate and Fe(III)-silicate complexes and nanoparticles in the survival of early cyanobacteria and photoferrotrophic bacteria

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Life evolved on Earth nearly four billion years ago, but the environmental conditions surrounding its evolution remains poorly understood. Ancient microbial fossil and isotopic records indicate the existence of thriving photosynthetic microbial ecosystems by 3.5 Ga, and perhaps as early as 3.8 Ga. However, these environments presented high levels of UV radiation and toxic iron concentrations that should have made early marine environments inhospitable to life. The answer to how ancient photosynthetic bacteria (photoferrotrophs and cyanobacteria) overcame these environmental stresses possibly lies in the composition of Archean seawater itself. High silica abundances in pre-2.5 Ga seawater may have been instrumental in the initial survival of ancient photosynthetic bacteria, as well as to the early colonization of littoral marine environments, by forming Fe(II)-silicate and Fe(III)-silicate complexes and nanoparticles in the ancient water column. These complexes and nanoparticles would have not only acted as a 'sunscreen' against the high levels in incident UV radiation. By complexing with iron(II), silica would have lowered the level of dissolved, bioavailable and toxic iron(II) to more manageable levels, thus enabling the survival and evolution of early bacteria under high iron conditions. In this regard, the purpose of this proposal is twofold: i) to identify the geochemical composition and physical nature of the Fe(II)-silicate and Fe(III)-silicate complexes and nanoparticles, and ii) to determine their ability at protecting freefloating (planktonic) cyanobacteria and photoferrotrophs from long-term exposure to Archean-level UV radiation. By applying information derived from the Archean rock record, to geochemical and biological models, this multidisciplinary approach will allow the elucidation of a number of important interactions between the early hydro-litho- and atmosphere, and early life.

#### Generation of Archean Granitoids and the Onset of Plate Tectonics.

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The formation of continental crust had a first order impact on the habitability of the Earth, being directly linked to the emergence of life and later allowing life to migrate onto land. Continents have a high elevation compared to oceans, because continental crustal rocks are granitic in composition and have a relatively low density compared to mantle rocks. It is generally accepted that these rocks must have formed by melting the mantle in a multi-step process that requires basalt and hydrous phases to be present. On the present-day Earth this occurs in subduction zones. Yet, in the Archean Earth, mantle temperatures were higher, more melt was produced in the mantle, and oceanic crust was significantly thicker. Models suggest that if mantle potential temperatures were 150-250K higher than present-day values, subduction could not have operated. Instead, parts of the crust may have dripped down into the mantle, a process known as sagduction. The question of whether plate tectonics operated in the Archean therefore depends on two key points: 1) that temperatures in the Archean upper mantle were so high that oceanic plates were unsubductable; 2) that Archean granitoids were produced by a process independent of subduction. How granites formed is incompletely understood, particularly for a warmer Earth. In this proposal, we will use petrological constraints to build a model of thick oceanic crust; one that is strongly differentiated with ultramafic cumulates in the lower half and hydrated basalt restricted to upper layers. We will also re-evaluate petrological constraints and cooling models that define temperatures in Archean ambient mantle. Then we will use 2D and 3D numerical models to simulate dehydration, melting and deformation within this crust and compare the results with available petrological/geochemical constraints. By including recently developed thermodynamic melting models and the chemical evolution of melts in the thermomechanical numerical models, we can use model predictions to test whether sagduction or subduction is a more efficient process to create granites.

In addition, we will derive parameterizations that describe the effect of both subduction and sagduction on the cooling of the Earth and include these in parameterized cooling models. This will give new insights in how such processes affect the thermal evolution of the Earth, how this affected crustal growth and on the timing of the onset of plate tectonics on our planet.

### Tracing back Earth building material: Identifying the perfect Ice, Dust, Pebble and Planetesimal Cocktail from simulations of the solar nebula

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This presentation will highlight results from the first funding phase. This concerns the newly developed "Two-Poppy" code [1], which is now one of our main tools to follow the formation of pebbles and planetesimals as we implemented for instance in the LIPAD code, based on our latest understanding of planetesimal formation [2]. We also report on the properties and mixture of planetesimals at the earth formation zone as well as the linked feeding zone from where that material is likely to originate. Besides the thesis work by Christian Lenz, this concerns also results from two bachelor theses by Marie Steinmeyer and Konstantin Gerbig. As the second part of the project we report on the progress we did with the implementation of planetesimal formation and pebble flux into the n-body simulations of planet formation using the LIPAD code.

I will also give an outlook on our project for the second funding phase. For the first project we plan to build in the chemical properties of dust, pebbles and planetesimals and the influence of a proper treatment of a time-dependent snow line on their distribution in time and space. For the second project we want to study the effect of collisions among Earth-Building Material on the chemical mix of Earth.

[1] Birnstiel, T., Klahr, H., Ercolano, B. 2017. TWO-POP-PY: Two-population dust evolution model. Astrophysics Source Code Library ascl:1708.015.

[2] Klahr, H., Schreiber, A. 2016. Linking the Origin of Asteroids to Planetesimal Formation in the Solar Nebula. Asteroids: New Observations, New Models 318, 1-8.



Figure 1: Spatial distribution of icy and pure rocky planetesimals as a result of a radially moving ice line. Test simulation from a bachelor thesis (Steinmeyer, Lenz, Birnstiel and Klahr, in prep.).

# In situ measurement of the Si isotope composition of metal and enstatite in reduced meteorites as a tracer for condensation processes and planetary differentiation during the early history of the Solar System Kodolányi<sup>\*</sup>, J.

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Enstatite meteorites, in particular metal-rich enstatite (EH) chondrites and aubrites, sampled regions of the early Solar System that show close isotopic resemblance to Earth, but differ from our planet chemically. They, and unsampled, but chemically and isotopically similar matter have been suggested to be the most prominent building blocks of Earth [1]. Enstatite meteorites are characterised by a reduced mineral assemblage which contains iron rich metal with a few weight percent (wt. %) silicon. The proposed project aims at constraining the silicon isotope composition of these metal grains, by means of in situ measurements using the NanoSIMS, and comparing these data with the silicon isotope composition of the meteorites' abundant enstatite and SiO<sub>2</sub> phases. Since silicon isotopes fractionate differently during the condensation of metal, than during the condensation of silicate phases [2], the results of the project should help us better understand the condensation conditions (e.g., T) of some of the most important components of enstatite chondrites, as well as disc-scale element- and isotope fractionation. Furthermore, the results will provide insight into the evolution of the silicon isotope system during the differentiation of reduced planetary bodies. Preliminary experiments established that silicon isotopes in metal with a silicon content of 1.2 wt. % or higher, can be measured with the NanoSIMS, using Faraday cups for detection. The signal-to-noise ratios allow <sup>30</sup>Si/<sup>28</sup>Si ratios to be measured with an uncertainty of 0.7 ‰, or better, on individual,  $20 \times 20 \,\mu\text{m}^2$  analysis spots on EH chondrite metal grains, which contain 2–4 wt. % silicon. Cooperation is planned with the German Research Centre for Geosciences (F. von Blanckenburg and J. Schüssler; characterisation of metal reference materials), the Friedrich Schiller University Jena (D. Harries; exchange of sample materials and sample characterisation), and in-house (J. Leitner; exchange of sample materials and sample characterisation). The latter two collaborators have active projects within SPP1833.

[1] Javoy, M. et al. (2010) EPSL 293, 259–268.

[2] Javoy, M. et al. (2012) EPSL 319–320, 118–127.

#### 3.2 Ga old microfossils in Moodies Group crinklies from the Barberton Greenstone Belt, South Africa

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A diverse assemblage of carbonaceous microstructures encrusted in anatase, interpreted as very probable microfossils to pseudomicrofossils, is present in the 3.32 Ga Moodies Group of the Barberton Greenstone Belt, South Africa. Similar associations of microstructures are present at the same stratigraphic level in outcrops more than 2 km apart. Three major microstructural types are present: thread-like, spheroidal and lenticular to spindle-like, which can be further subdivided into several sub-types (Fig. 1). Most of the microstructures were deposited as part of an assemblage of clastic sediments. Some specimens occur in colony like accumulations and seem to have formerly had elastic but fragile walls. Size distributions for the three types are mostly constricted, a feature characteristic of biogenic assemblies. The microstructures are composed of disordered carbon (as revealed by Raman spectroscopy) and are encrusted in anatase (TiO<sub>2</sub>). The combined morphological and geological evidence suggests that the structures are likely to very likely fossil remains of microorganisms. The morphological variety among the microstructures suggests that a diverse microbial ecosystem flourished in the Moodies Group during the Archaean.



Figure 1. Four different kinds of microfossils.

#### Stable tungsten isotope compositions of Earth's oldest rocks

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The geochemical cycle of W in the crust/mantle system and in the modern/ancient low-temperature environments is so far poorly understood. Tungsten stable isotopes represent a potential tool to better constrain this cycle, because of W isotope fractionation during redox-changes (W occurs in the valance states +4 and +6) and during coordination changes in the course of adsorption reactions of aqueous WO42-. First tungsten stable isotope studies on terrestrial reference materials yielded inconsistent results [1, 2, 3], which highlights the analytical challenge for sufficiently accurate measurements. We employed a newly calibrated 180W-183W double-spike to assess natural mass-dependent isotope fractionation and to correct for fractionation induced during chemical purification and mass spectrometric measurement. Measurements of several different rock reference materials span a total range in  $\delta$ 186/184W of 0.150 ‰ at a resolution of ±0.018 ‰ (2 s.d.) [4]. Our results for reference materials are only consistent with those of [3], but contradict with [1] and [2]. First stable tungsten isotope measurements of rocks from Isua, Greenland, which are of Eoarchean age, range between -0.041 and +0.206 in  $\delta$ 186/184W. Thus, our resolution of ±0.018 ‰ allows the discrimination between different Eoarchean W reservoirs. Isotopic differences might result from stable W isotope fractionation during magmatic differentiation. Alternatively, the mobilization of W in Isua rocks by hydrothermal and/or magmatic fluids might be accompanied by isotope fractionation.

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[2] Abraham et al. (2015) J. Anal. At. Spetrom. 30, 2334-2342.

[3] Krabbe et al. (2017) Chem. Geol. 450, 135-144.

[4] Kurzweil et al. (2018) Chem. Geol. 476, 407-417.

### Tracing the development of early Earth's biosphere by systematic characterization of kerogens preserved in the Archean rock record

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Bacteria have inhabited our planet since at least 3.5 billion years ago (Ga) and oxygenic photosynthesis must have existed by 2.45 Ga, since at this point in Earth history rare sulfur isotopes record the first increase in atmospheric oxidation [e.g. 1]. But we still don't know when oxygenic photosynthesis first emerged; neither do we know the composition of the Archean biosphere or how it changed upon incipient environmental oxygenation. Yet this information is of high relevance for physico-chemical models of the early Earth system, for our understanding of the tempo and mode of atmospheric oxygenation, for contextualizing the observed Archean rearrangement of biogeochemical cycles and lastly for our fundamental understanding of the nature of Earth's earliest biosphere. With exceptionally sparse microfossil occurrences of complicated taxonomic association [e.g. 2], and the recent finding that Archean rocks have far exceeded the temperature threshold for the preservation of biologically diagnostic biomarker hydrocarbons [3], our only avenue to reconstructing Earth earliest biosphere involves bulk characteristics of sedimentary organic matter—i.e. kerogen—that (i) cannot be contaminated and (ii) whose structural and compositional changes with increasing thermal maturity are known. In this project we propose to shed light on Earth's earliest biology by studying the bulk chemical composition (N/C, S/C), internal structure (in particular aromaticity), and stable carbon isotope dynamics ( $\Delta\delta^{13}$ C of kerogen and alkanes released by pyrolysis) of Archean kerogen after normalization to varying degrees of thermal overprint as determined by the H/C ratio and Raman-spectroscopic characteristics of kerogens [4]. The separate consideration of platform and basinal environments in high stratigraphic resolution throughout the Archean will allow us to perform statistics and determine the relevance of observed changes, thereby revealing if and when a shift in the composition of preserved biomass took place. The maturity-normalized internal structure of the kerogen, studied by solid state NMR, has the capacity to indicate at what point during the Archean, microaerobic environments started affecting the preservation of organic matter. Lastly the stable carbon isotopic offset between kerogens and indigenous alkanes (released by pyrolysis) can reveal details of the Archean ecosystem structure and the extent of heterotrophy [e.g. 5]. Overall the here presented systematic approach is thorough, novel and expected to significantly increase our understanding of Earth earliest biosphere. In addition, we may gain information on localized trace abundances of environmental oxygen affecting the diagenesis of organic matter, thereby placing new and better constraints on the emergence of oxygenic photosynthesis.

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- [2] French, K. et al. (2015) PNAS 112, 5915-5920.
- [3] Javaux, E. et al. (2010) Nature 463, 934–938.
- [4] Ferralis, N. et al. (2016) Carbon 108, 440-449.
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### Isotopic, chemical and mineralogical characterization of organic and inorganic nitrogen-carriers in chondritic meteorites

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Nitrogen is the most abundant component in Earth's atmosphere and one of the key elements for the evolution of Earth's biosphere. However, the types of nitrogen carriers, their abundances and nitrogen isotopic compositions are not well constrained for all potential terrestrial building blocks. We investigated the N-isotopic compositions of 56 organic matter (OM) aggregates (2–45 μm in size) in the CR chondrites MIL 07525, Renazzo, and EET 92161 by NanoSIMS. Enrichments of up to ~900 % in 15N were found, exceeding the typical  $\delta$ 15Nbulk of 120-230 % for CR OM. Sixteen aggregates show (multi-)globular morphologies, where layers with isotopically highly anomalous N (δ15N ~700–2,000 ‰) alternate with areas showing  $\delta$ 15N of 50-300 ‰. This gives strong support for OM formation/modification as well as redistribution of 15N-bearing molecules by (episodic) fluid interactions on the parent body. We also investigated silicon nitride (Si3N4) and osbornite (TiN) inventories of several enstatite chondrites (ECs), which could have contributed to the Earth's building blocks based on isotopic similarities. Si3N4 has light N-isotopic composition with  $\delta$ 15Navg = (-62±1) ‰, significantly lighter than both reported N-isotopic compositions for bulk ECs and sinoite (Si2N2O). Si3N4 abundances are too high to be explained by exsolution from the metal on the parent body; instead, our findings support formation under Solar nebula conditions. TiN in Neuschwanstein (EL6) has an average  $\delta$ 15N of -30 ‰, compatible with the average N-isotopic compositions of bulk ECs and Si2N2O from EL chondrites. Abundance estimates indicate that TiN is apparently not a major N-carrier in the enstatite chondrites, contrasting established assumptions. Our findings for the OM indicate hydrous parent body processes played an important role for the formation of organic N-carriers delivered to early Earth. Moreover, the carrier phase for the majority of N in ECs is still to be identified, with Fe,Ni metal or sulfides being the best candidates so far.

On the effects of planetary rotation on early Earth differentiation: Spherical shell model Maas\*, C., Hansen, U. WWU Münster, Institute for Geophysics, Corrensstraße 24, 48149 Münster, Germany christian.maas@uni-muenster.de

Several giant impacts during the later stage of the Earth's accretion caused one or more deep terrestrial magma oceans of global extent. During that time, the Earth rotated very fast with a rotation period between two and five hours. Owing to the small magma viscosity of the vigorously convecting magma ocean, planetary rotation probably had a profound effect on the magma ocean solidification and the early differentiation of the Earth. Accordingly, the effect of planetary rotation is not only of key importance for the chemical structure and the development of chemical heterogeneities on Earth but also sets the stage for the onset of plate tectonics. In this work we investigate the influence of planetary rotation on the early magma ocean crystallization using a spherical shell model. Our results show that without and at slow planetary rotation, crystals are kept in suspension everywhere in the spherical shell. In contrast, at moderate rotation rate clear dependencies on latitude do arise. Here, crystals settle at the poles and are kept in suspension at mid-latitude but accumulate in the bottom half at the equator. At faster rotation rate, all crystals accumulate in the equatorial region. All in all, our numerical experiments demonstrate the possibility of an inhomogeneous solidification of a terrestrial magma ocean with respect to time and latitude, favouring the development of large scale chemical heterogeneities.

### 3.35 Ga carbonate interstitials from the Pilbara terrane, Australia, indicate unradiogenic <sup>87</sup>Sr/<sup>86</sup>Sr isotope composition of the Archean seawater

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Carbonate rocks occur rarely in early Archean greenstone belts. Primary interstitial carbonates within pillow lavas are even more rare, and they are remnants that represent important records for reconstructing the composition of ancient oceans and the atmosphere [1]. Furthermore, carbonates are strongly susceptible to secondary alteration and are therefore a useful tool for better investigating metamorphic, diagenetic and hydrothermal events.

Here, we present preliminary Sr isotope data for 10 carbonate interstitials, cavity fillings, and veins of the Euro, Apex, Mt. Ada, Honeyeater and Whundo units (3.5 - 3.1 Ga) of the Pilbara terrane. Diluted acetic acid leachates from these carbonates reveal that two microcrystalline calcites (Euro, 3.35 Ga; Whundo, 3.13 Ga) exhibit markedly low <sup>87</sup>Sr/<sup>86</sup>Sr isotope composition between 0.7010 and 0.7013 coupled with high Sr concentrations of >800 ppm. In contrast, coarse grained carbonates exhibit lower Sr concentrations (20 - 50 ppm), combined with more radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr between 0.7023 and 0.7159.

The Sr dataset of the primary calcites indicates Sr isotope composition of ca. 0.7010 for Archean seawater at around 3.35 Ga. Secondary alteration has led to replacement of primary carbonate minerals, which caused the mobilization of Sr and the overprinting of the <sup>87</sup>Sr/<sup>86</sup>Sr budget towards more radiogenic values.

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### The rise and fall of Archean atmospheric oxygen: did temporary carbon burial as Fe(Ox) -DOM complexes play a modulating role?

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The bioavailability of molecular oxygen is still considered to be the principal driver for the evolution of increasingly complex organisms. After the first rise of atmospheric oxygen (i.e. the Great Oxidation Event; GOE), around 2.5–2.3 Ga, life's evolution appears rather sluggish before picking up pace at the end of the Ediacaran. While the GOE is temporally well constrained, less is known about the subsequent evolution of Earth's oxygen budget. Redox-sensitive metals actually suggest that atmospheric O<sub>2</sub> levels may have dropped again after the GOE. It has long been known that the oxidation state of Earth's surface environments is tightly coupled to the carbon cycle. In order for the atmosphere to receive a boost in O<sub>2</sub> content, some primary production in the surface ocean must escape short-term recycling and become buried long-term in sediments beneath the sea floor. We suspect that massive deposition of banded iron formations may have played a relevant role.

### Modeling the evolution of the parent body of acapulcoites and lodranites: A case study for partially differentiated asteroids

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The acapulcoites and lodranites (AL) are rare groups of primitive achondritic meteorites. Although they have the texture of achondrites, they are compositionally closely related to ordinary chondrites. Several characteristics such as unique oxygen isotope composition and similar cosmic ray exposure ages indicate that these meteorites originate from a common parent body<sup>[1,2,3]</sup>. By contrast with both chondrites and achondrites, AL meteorites are especially interesting because they experienced partial melting and only minor melt segregation<sup>[4]</sup>. Unravelling their origin contributes directly to the understanding of the early differentiation stage of planetary objects in the Solar system. The information preserved in the structure and composition of meteorites can be recovered by modeling the evolution of their parent bodies and by comparing the results with the laboratory measurements, e.g., closure ages and temperatures. In this study, we investigate the thermal and structural evolution of the parent body of the AL meteorites using a combination of two models that consider compaction, partial melting as well as metal-rock differentiation, and provide best fit estimates for the parameters that define key properties of the parent body. We compare the model calculations with the maximum metamorphic temperatures, the differentiation degree and the thermo-chronological data available. We obtain a consistent set of parameters that fits the available thermo-chronological data for the members of the AL-clan. Our models provide estimates of the size, formation time, orbit of formation, nature of the precursor material and internal structure of the AL parent body. Our results indicate a considerably larger size of the parent body than previous models<sup>[5,6]</sup>. A partially differentiated structure indicates, further, that AL meteorites could share a common parent body with differentiated stony and iron meteorites.

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- [3] Eugster, O. and Lorenzetti, S. (2005) GCA 69, 2675-2685.
- [4] McCoy, T. et al. (1997) GCA 61, 639-650.
- [5] Touboul, M. et al. (2009) EPSL 284, 168-178.
- [6] Golabek, G. J. et al. (2014) MAPS 49, 1083-1099.

### Modelling of accretion and differentiation of Earth's building blocks: Ice-rich precursors and their retention of water Neumann\*, W.

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The building blocks of the Earth are represented by a variety of small bodies, most of which are clustered in belts, but some of them move on distinct orbits (e.g. NEAs, comets) or are satellites (icy moons). Small bodies cover a spectrum of compositions in terms of H<sub>2</sub>O content, ranging from dry objects (Vesta) to those that contain a high H<sub>2</sub>O fraction in a distinct layer (Ceres, Enceladus). Both types (e.g. Vesta, Ceres) are found in the asteroid belt; bodies of the second type are also found in the outer solar system (e.g. Enceladus, Charon).

The present project will focus on those potential precursors of the Earth that contain a substantial water fraction, e.g., planetesimals with CC composition, Kuiper Belt Objects (KBOs) and icy moons. Specific objects of this very diverse set of bodies that were observed by space missions are the dwarf planet Ceres, the icy moon Enceladus and various KBOs (e.g. Charon). To this end, the thermal, structural and chemical evolution of water-rich building blocks of the Earth, the conditions for the retention of water, and the likelihood of the delivery of H<sub>2</sub>O to the Earth by different classes of objects will be addressed. Chemical and physical processes influencing the water-rock separation will be studied. Several models for rocky and icy planetesimals and planetary embryos were developed previously<sup>[1-5]</sup>. On the one hand, we will expand our newly derived model<sup>[4]</sup> to further consider processes such as flux of water vapor, reduction of the dust porosity, hydration and dehydration reactions, and tidal heating. Further enhancements will be the consideration of liquid-state convection and hydrothermal circulation to better constrain the cooling behavior of water-rich precursors. On the other hand, we will adopt the 3D thermal convection code GAIA<sup>[6]</sup> to investigate the implications of the solid-state convection. The aim is to find likely evolution scenarios and interior structures of different classes of ice-rich building blocks of the Earth, depending on their composition and formation time relative to the calcium-aluminum-rich inclusions, and to investigate whether and how they could retain water and were able to deliver it to Earth. Preliminary results for the dwarf planet Ceres and the icy moon Enceladus will be presented.

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#### **Global volatile cycles on early Earth**

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This poster will summarize the project of a same-named proposal for the second funding period of the SPP 1833. While Earth is a planet where for present-day processes in the interior and at the surface we have a wealth of information, data for the early evolution of the planet is sparse. Apart from few zircon inclusions that date back to Hadean times, first rock samples are limited to the end of the Eoarchaean and to the Archean time. These rock samples, while providing interesting single observations of early Earth's surface, are only some pieces of a much larger puzzle that we still need to solve to be able to explain why Earth developed to the unique habitable planet that we know. Geological measurements therefore should be complemented by computational models to interpret the geological record in a global context, and to be able to constrain evolution scenarios of early Earth. In the proposed project, the PhD student will enhance a thermo-chemical model of Earth's mantle, lithosphere and crust by including volatile cycles (focussing mainly on H, C and N that form greenhouse gases, but also Xe, Ar and Ne as trace elements) from interior to surface and vice versa. The cycles operate via outgassing, condensation and crustal recycling. We will then compare our model predictions with respect to volatiles to the collected early Earth data. Such a model approach allows to investigate the evolution of volatile reservoirs and isotope relations over time. Using a Monte-Carlo method, we will then model different evolution scenarios for early Earth for random initial thermal and compositional states of Earth's interior after the Moon-forming impact. The resulting evolution scenarios can be compared to various field data from different times. Constraints set by the Archaean geological record can also help to indicate how the earliest evolution of Earth needed to evolve to explain the later available geological and geochemical samples.

#### Constraining the composition of Earth's late stage building blocks from the earliest ultramafic rocks

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Earth was built by the accretion of planetesimals and had differentiated into a metal core and silicate mantle probably within the first <100 Myr after the birth of the solar system [1]. The final ~1% of planetesimals that accreted did not equilibrate with the core and are commonly referred to as the "late veneer". It has been suggested that this late veneer was the dominant source of volatile elements and water (H2O) on Earth, closely linking the late accretion stage to the origin and sustaining of life [2]. The evidence for a volatile-rich late veneer, however, has been disputed [3]. Here, we will constrain the compositions of Earth's late stage building blocks by studying the triple oxygen (O) isotope compositions of Archean ultramafic rocks that formed before their mantle sources had received a late veneer component. Oxygen isotopes show large mass-independent variations between different types of meteoritic materials and late accretion by different types of meteoritic materials consequently would have had distinct imprints on the O isotope composition of the mantle. Comparing the O isotope compositions of the pre- and post-late veneer mantle thus allows reconstructing the types of meteoritic materials that dominated the final ~1% of Earth's accretion history – and constraining whether these were volatile-poor and dry or volatile-rich and wet. In order to verify the pre-late veneer origin of the mantle sources from our samples we will also study their platinum (Pt) and tungsten (W) isotope compositions, which were previously demonstrated to be powerful tracers for the absence of a late veneer component in the Archean mantle. In order to avoid the effects of secondary processes that may have obscured the O isotope compositions of Archean samples, e.g., weathering, metamorphism, magmatic assimilation and crystal-chemical processes, we will focus on the analysis of sufficiently pristine mineral separates, predominantly olivine, and carefully inspect major and trace element variations in the sample suites for indications of such processes. In total, five distinct sample suites of Archean ultramafic rocks will be studied that range in ages from >3.81 Ga to ~2.7 Ga. Some preliminary results for some of these suites are presented.

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- [3] Fischer-Gödde & Kleine 2017 Nature 541(7638), 52

#### **Plume-Lithosphere interaction during Archean**

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There are many open issues regarding the continental crust generation during Archean, and most of them are focusing on the application of uniformitarian models (i.e. magmatic arc-system), or on vertical deformation triggered by mantle plumes. The plume model has become more popular recently, but it cannot be tested using geological and geochemical data alone, and numerical modelling is required to understand the physical and chemical processes behind it. Numerical modelling together with petrological forward modelling have been useful tools to understand Archean dynamics, but the bulk of the work on such topic neglected the third dimension. Therefore, many important features related to the magmatic processes, such as the structure of the primordial continental crust and the interaction of the plume with the lithosphere have been hampered and are not yet fully explored. Here we show our preliminary work on the plumelithosphere interaction using Archean like conditions, combining the state-of-the-art of the thermodynamic modelling with the 3D petro-thermo-mechanical code LaMEM. As part of the preliminary work, we focus on the effect of a rising plume on the lithosphere. We will test whether it can promote a tectono-metamorphic deformation of the primordial crust and whether it can potentially affect the stability of the crust and trigger drips and delamination. We also compare the 3D with earlier 2D results.

#### Fate of carbon during early differentiation of the Earth Posner\*, E., Blanchard, I., Rubie, D.C. Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany \*esther.posner@uni-bayreuth.de

During the Hadean Eon, the early Earth was heavily bombarded by numerous planetesimals and a smaller number of planetary embryos. The high energy associated with these impacts during accretion of the Earth was sufficient to generate global magma oceans that allowed for the segregation of dense iron-rich metallic liquid from molten silicate to form the Earth's core. Carbon, an abundant volatile and essential building block for life on Earth, is also siderophile ('ironloving') and, as a consequence, its fate in a magma ocean involves escape into both the early atmosphere and coreforming liquids. The primordial distribution of carbon between the primary terrestrial reservoirs (core, mantle, atmosphere) establishes a baseline or starting point from which further volatile cycling between the mantle and the atmosphere would proceed. We therefore aim to better constrain the partitioning and transport behavior of carbon in a magma ocean, which is required for integration into more broad astrophysical and geodynamic models. We first address geochemical equilibrium in a magma ocean by determining the partitioning behavior of carbon between silicate liquid and molten iron. Second, we employ a kinetic approach by determining mass transport properties (viscosity, diffusivity) of both carbon-bearing and carbon-free peridotite liquid, in addition to carbon transport in liquid iron. With the newly obtained data, carbon distribution between core, mantle, and early atmosphere upon crystallization of the final magma ocean is modeled by combining carbon transport and partitioning data with accretion sequences derived from N-body simulations that produced an Earth-like body with accurate proportions and radial distance. A range of scenarios are investigated by varying the following parameters: (i) magma ocean depth; (ii) degree of chemical equilibration between metal-silicate; and (iii) initial bulk carbon of precursory material based on the chemistry of carbonaceous chondrites.

#### **Early Archean Carbon Archives**

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Understanding the interplay between biological and geological processes on the early Earth is one of the most challenging endeavors of current geobiological research [1]. Given that all extant life on Earth is based on carbon, carbon compounds could help to trace life and metabolic processes on the early Earth. Important carbon archives include carbonate minerals (in various facies) and organic matter (particularly in "Black Chert Veins" and "Black Barites"). The newly proposed projects aim at deciphering these archives to better understand carbon cycling in Early Archaean times.

One of the proposed projects (RE 665/44-1) focuses on c. 3.6–3.3 Ga carbonates from the Pilbara region (Western Australia). Little is known so far about the formation pathways of these precipitates. Most of the carbonates (mainly calcites) were precipitated in inter-pillow spaces of the greenstone belts. These precipitates exhibit  $\delta$ 13Ccarbonate values of ~0‰, which is in the range of modern sea water. The precipitation was probably driven by a constant enrichment of cations (Ca2+, Mg2+ etc.) via water/rock interactions (e.g. in the glassy hyaloclastite zones of the pillow margins). The c. 3.5 Ga-old Dresser Formation includes rare organic-rich sedimentary carbonates (Mn-rich dolomites/kutnahorites). These precipitates exhibit  $\delta$ 13Ccarbonate values of c. –6‰, pointing to an endogenic carbon source (e.g. hydrothermal CO2). These carbonates therefore most likely represent microbialites that formed under low temperature hydrothermal conditions. The c. 3.4 Ga-old Strelley Pool Formation contains various microbial mat facies [2]. Particularly important for this project are dolomitic stromatolites, whose formation was probably controlled by extracellular polymeric substances (EPS). These dolomites are characterized by heavy  $\delta$ 13Ccarbonate-values of c. +5‰, which is in good accordance with the presence of photosynthetic metabolisms in the microbial mat.

A second project focuses on organic matter in Archean "Black Chert Veins" and "Black Barites". In both cases, the origin of this organic carbon is uncertain (biotic vs. abiotic). In a first project (DU 1450/3-1), we were analyzing kerogen contained in a hydrothermal chert vein from the c. 3.5 Ga-old Dresser Formation [3]. Catalytic hydropyrolysis (HyPy) of this kerogen yielded n-alkanes up to n-C22, with a sharp decrease in abundance beyond n-C18. This distribution ( $\leq$  n-C18) is very similar to that observed in HyPy products of recent bacterial biomass, whereas it differs markedly from the unimodal distribution of abiotic compounds experimentally formed via Fischer-Tropsch-type synthesis [3,4]. We therefore propose that the organic matter in the Archean chert veins has a primarily microbial origin. The microbially-derived organic matter may have accumulated in anoxic aquatic (surface and/or subsurface) environments, and was then assimilated, redistributed and sequestered by the hydrothermal fluids ("hydrothermal pump hypothesis"; [3]).

We are going to test this hypothesis in the frame of a newly proposed project (RE 665/42-2; DU 1450/3-2; TH 713/13-2). We will furthermore explore organic matter in hydrothermally derived "Black Barites" that are commonly closely associated with the "Black Chert Veins". Bedded barite units often include stromatolitic structures consisting of pyrite and sphalerite laminae as well as tiny carbonate crystals. These precipitates are characterized by unusually low  $\delta$ 34Ssulfide and  $\delta$ 13Ccarbonate signatures ( $\delta$ 34S -15‰ sulfides,  $\delta$ 34S +5‰ barite,  $\delta$ 13C -18‰,  $\delta$ 18O 10‰) clearly pointing at biological cycling of biogenic elements. The barites are interspersed with abundant primary fluid inclusions loaded with low-molecular weight gases (e.g. CH4, H2S, CS2) which may represent an unprecedented archive for the chemical ingredients providing the basis of the very first microbial metabolisms.

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### Non-detrital Gallium and Aluminum in Early Precambrian Marine Chemical Sediments and the Potential Use of the Ga/Al Ratio as a Geochemical Proxy for Metal Sources and Relative Fluxes to the Early Ocean

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Based on the differences in Ga/AI ratios between continental runoff (low Ga/AI) and high-temperature hydrothermal fluids (high Ga/AI) it may be possible to distinguish terrigenous from mantle-derived sources of Ga and AI in Precambrian seawater assuming that no major fractionation of the element pair occurs during precipitation of marine chemical sediments such as banded iron formations (BIFs).

Lately, high and low Ge/Si ratios in Fe- and Si-rich BIF bands, respectively, have been interpreted to reflect the interaction of two compositionally different water masses and, therefore, pointing towards decoupled sources of Fe and Si in the Precambrian ocean based on the same principle as described above for Ga/AI [e.g. 1]. However, Ge has also been found to preferentially sorb onto Fe-oxyhydroxides, leading to a fractionation of the Ge-Si pair in the presence of the latter [2], which may provide an alternative explanation for high Ge/Si ratios in Fe-rich BIF bands [3]. Ga/AI ratios have the potential to distinguish between these two contradicting interpretations of Ge/Si ratios: If the banding of BIFs indeed represents alternating periods of increased high-temperature hydrothermal input (Fe-rich bands) and times during which seawater chemistry was dominated by input of continentally derived solutes (Si-rich bands), this should be accompanied accordingly by changes in the Ga/AI ratios in adjacent BIF bands. Fe-rich bands should be characterized by high Ga/AI ratios, Si-rich bands, on the other hand, should show low Ga/AI.

Developing and applying Ga/AI ratios as a proxy for the sources of non-detrital Ga and AI in BIFs would, therefore, be a valuable contribution to a better understanding of the precipitation mechanisms of one of the most abundant and important types of ancient marine chemical sediments, and may be a straightforward approach to verify the application of Ge/Si ratios as geochemical source proxies.

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

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The preservation of geologic materials from the early period when Earth became a habitable planet is precarious. Only rare examples of detrital zircon crystals have escaped obliteration since the Hadean eon. These crystals also host a rich inclusion assembly which attests to their formation conditions. The presence of light carbon isotopic compositions of graphite inclusions in Hadean zircon has been interpreted to indicate an early emergence of terrestrial life. We aim to follow up on this discovery by investigating graphite inclusions in minerals from post-Hadean granites by (1) devising criteria which can aid in identifying post entrapment disturbance of inclusions, and (2) constraining how graphite in igneous rocks relates to biogenic carbonaceous materials, and how these materials contribute to magmatic carbon budgets. The proposed research will, for the first time, use correlated micro-analytical imaging and high spatial resolution mass-spectrometry techniques to resolve the origins of graphite in magmatic rocks, especially as inclusions. Insights gained from two S-type granite locations in zircon. The methodologies we plan to develop will be implemented in a collaborative search for additional carbonaceous inclusions from the Hadean by an international research consortium, which currently has succeeded in identifying the largest number of Hadean zircon crystals worldwide.

#### Large-scale fold structures of the Barberton Greenstone Belt, South Africa & Swaziland

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Despite decades of intense investigation and a continuing debate about the style of tectonic processes, which led to the formation and subsequent deformation of the Barberton Greenstone Belt [1, 2], the large-scale fold structures of the interior of the belt are still poorly understood. One of the characteristic features of the synclines, which almost exclusively make up the interior of the greenstone belt, is their steeply, doubly plunging fold axis. The surface geometry of these folds implies a depth of >25 km for some of these structures, which contradicts geophysical data. Furthermore, a higher metamorphic overprint for the deeper part of the folds would be expected, which cannot be validated in any place. Possible explanations for this conflict are (1) decreasing primary sedimentary thickness towards the center of the respective syncline. This hypothesis is supported by paleocurrent data and facies architecture indicating the presence of deltas at the synclines' margins. (2) tectonic repetition, which places parts of the syncline, which should be deeper according to the surface geology, adjacent to the uppermost parts of the fold due to reverse faulting. While evidence for this hypothesis is rare, it cannot be excluded, that these reverse faults are defined today by a swarm of doleritic dykes, which can be found all across the greenstone belt. It can be reasonably assumed that these dykes have risen along weak zones, which may have been created through earlier faulting.

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- [2] De Wit, M. et al. (2017) Geoscience Frontiers

**The origin of komatiites and basalts of the lower Onverwacht Group, Barberton Greenstone Belt (S Africa)** Schneider, K.P.\*, Hoffmann, J.E., Münker, C., Patyniak, M., Sprung, P., Roerdink, D., Garbe Schönberg, D., Kröner, A. \*Institut für Geologische Wissenschaften, Malteserstraße 74-100, D-12249 Berlin, Germany Kathrin.schneider@fu-berlin.de

Studying the origin of Archean mantle-derived rocks is crucial for our understanding of the geodynamic processes that operated on the early Earth. To elucidate the origin of the extraordinarily well preserved mafic-ultramafic rocks from the 3.55 to 3.45 Ga lower Onverwacht Group of the Barberton Greenstone Belt, we present a comprehensive dataset of major and trace element data as well as Lu-Hf and Sm-Nd isotope compositions for a variety of metavolcanic rocks. Primitive mantle normalized trace element patterns of well-preserved komatiites and basalts are generally flat, with slightly depleted heavy rare earth elements and Th, suggesting high degrees of melting of a primitive mantle source containing residual garnet. Conversely, Lu-Hf and Sm-Nd whole-rock isotope systematics indicate an overall depleted nature of the rocks. Based on the current data set, in combination with previously published data, we interpret the komatiite melts to consist to a major part of high degree melts of depleted mantle that is similar to modern depleted MORB mantle. These high degree depleted mantle melts. In our proposed model, the tholeiitic basalts are formed via fractional crystallization from the komatiitic melts. Our geochemical model is in agreement with recent numerical geodynamic models [1,2,3] that propose interaction of a partially molten layer within the Archean upper mantle with more primitive plume-derived melt, leading to thinning of the lithospheric mantle, contemporaneous with extensional rifting.

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### Isotopic investigations of the pre-Great Oxidation Event (GOE) geo-biological evolution (project 1) and the mode of atmospheric oxygen build-up at the GOE as a sharp or an oscillating process (project 2)

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There is growing (isotope) geochemical evidence for the existence of locally stratified basins with oxidized ocean surface water masses – generally called oxygen oasis - as early as 2.95 billion years ago [1-3]. This is 500 million years before the first evidence that the atmosphere became significantly oxidized to ca. 1-3 % of its present atmospheric level (PAL) of oxygen during the ~2.4 byrs Great Oxidation Event (GOE). It is generally accepted amongst these geochemical studies that the early pre-GOE oxygen production in the Mesoarchean oceans was the result of oxygenic photosynthesis by Cyanobacteria, which potentially facilitated the onset of aerobic respiration in the microbial realm. Microbiologically, however, such an early onset of cyanobacterial photosynthesis is highly controversial and the recent study of Soo et al. (2018) [4], investigating genomes of different classes of Cyanobacteria, showed that many of these lack the photosynthetic machinery, that phototrophy was not an ancestral feature of Cyanobacteria and that *Oxyphotobacteria* acquired the genes for photosynthetis relatively late in cyanobacterial evolution. As such, the exact temporal onset of oxygen production by cyanobacterial photosynthesis and the resulting mode of oxygenation of the oceans and the atmosphere still remain elusive to the biogeological community. Similarly, the timing and mode of the evolution of other respiratory processes in Early Earth's history, such as methanogenesis, are still poorly constrained mainly due to the lack of biomarkers in ancient sediments capable of surviving diagenesis and metamorphism.

In project 1 of the second phase of SPP 1833 we would like to explore the potential of stable Ni isotopes to trace biogeochemical activity in Paleo- to Mesoarchean sediments. Preliminary data show that fractionation of Ni stable isotopes by methanogens may hold great promise as a potential biomarker and could reveal significant clues to understanding the Earth's early biosphere.

Previous investigations of paleo-proterozoic sediments from the Rooihoogte/Duitschland and Timeball Hill formations of the Transvaal and Griqualand West sub-basins (Transvaal Supergroup, South Africa) revealed a sharp transition from mass-independent to mass-dependent fractionation of S-isotopes and thus onset of an oxygenated atmosphere 2.32 billion years ago (i.e. MIF-S to MDF-S) [5-7]. Recent dating of sills in the Griqualand West sub-basin, however, demanded significant readjustment of the correlation of some of the formations in the two sub-basins of the Transvaal Supergroup [8]. This readjusted correlation, if temporally correct, does now allow for repeated transitions of MIF-S to MDF-S and thus an oscillating oxygen build-up in the atmosphere.

In project 2 of the second phase of SPP 1833 we would like to investigate whether the build-up of free atmospheric oxygen at the GOE was a sharp or an oscillating event by measuring stable isotope variations of the redox-sensitive transition metals Mo and Se on sediments from new drill-cores throughout the full stratigraphy of the Rooihoogte/Duitschland and Timeball Hill formations.

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#### Effects of compressibility and non-linear rheology on the early dynamics of the solid mantle

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The crystallization of the magma ocean is supposed to end up with a gravitationally unstable density stratification of the mantle [1]. As a consequence, the onset of mantle convection is largely driven by a compositional overturn rather than by thermal buoyancy. Upon overturn, dense cumulates sink at the core-mantle boundary partly mixing with the surrounding material [2]. Various factors such as the level of density stratification and the rheology affect the overturn time-scale and whether or not mantle convection can set in after the overturn is completed [3, 4]. We will give an overview of the numerical approach that is generally applied in the geodynamic modeling community to treat this problem and outline its limitations, arguing for the need to consider a more careful treatment of mantle convection equations will be presented. In addition, we will discuss the effects of non-Newtonian rheology in driving the compositional overturn.

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### Habitability of primordial "soups" using modified Miller-Urey experiments and state-of- the-art analytical tools Schulze-Makuch\*, D., Ruf, A., et al.

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There is much evidence that Earth became geologically habitable soon after its formation and developed oceans early on, however, the chemical habitability of the primordial ocean has not been investigated thus far. Thus, we propose to conduct improved Miller-type experiments that consider the latest understanding of the physicochemical conditions that prevailed on early Earth, including an influx of organic material from space. Furthermore, we simultaneously allow anaerobic microorganisms contained within the closed system of our Miller-type experimental setup to thrive off the prebiotic molecules continuously being produced abiotically. With these experiments we investigate a Miller-type primordial soup with the purpose to (a) better understand its chemical complexity, particularly with respect to organic molecules, (b) decipher the potential relevance of the geological environment and extra-terrestrial organic material delivered by meteorites, and (c) investigate the habitability of such a chemical environment in relation to modern organisms.



Biotic Miller Experiment (this study)



Fig.: Schematic representation of the "classical" Miller Experiment set-up and the experimental set-up proposed for this study. Prebiotic molecules are formed in the boiling solution (a) and during spark discharge (b). Anaerobic heterotrophs are cultured in an additional vessel (c) that is continuously supplied with the prebiotic "soup".

#### Origin of volatiles and organics on Earth, IDPs, meteorites, and comets

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One of the most intriguing scientific questions is to understand conditions at which our planetary system was born and how Earth became habitable. To answer these questions, one has to first understand the evolution, distribution, and abundances of the key ingredients for life – water, carbon-, and nitrogen-bearing compounds in the solar nebula, in what form they existed, and how they have been delivered to Earth. The important clues to the physical conditions and chemical complexity in this ancient epoch are hidden in the chemical and isotopic composition of Earth surface volatiles and primitive bodies of the solar system such as meteorites, comets, and interplanetary dust particles. It is challenging to relate the mineralogical, chemical, and isotopic composition and water content revealed by laboratory investigations with the conditions in the young solar system at about 4.57 Ga ago, unless a feasible evolutionary model of the solar nebula is used. In my talk, I will present a detailed model of the solar nebula that includes gas and dust structures, turbulent mixing, high-energy radiation, and gas-grain time-dependent chemistry with deuterium fractionation. Using this model, the distribution and evolution of water and major C-bearing molecules and their D/H ratios in the solar nebula are computed and related to the pristine reservoirs of planetesimals and comets that seeded the early Earth and could have made it habitable.

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#### Noble gas state of the Archean mantle

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A significant fraction of the terrestrial atmosphere originated by degassing of the Earth's mantle very early in Earth's history. This fundamental conclusion is mainly derived from the excess of radiogenic isotopes, e.g. <sup>40</sup>Ar from <sup>40</sup>K and more stringently <sup>129</sup>Xe from decay of short-lived <sup>129</sup>I, along with fission Xe from <sup>238</sup>U and / or <sup>244</sup>Pu. While the present-day mantle isotopic state is quite well known, there is hardly information about the Archean mantle. The ancient mantle is expected to have contained a higher proportion of primordial and lower proportion of radiogenic nuclides, depending on - and therefore constraining - the degassing history and lithophile parent nuclide depletion of Earth's mantle. However, there are only a few helium isotopic data on Archean mantle rocks, and it is uncertain to what degree cosmogenic nuclides may compromise isotopic data. Here we propose to analyse Archean ultramafic rocks from peridotite lenses of the Itsaq Gneiss Complex south of the Isua Supracrustal belt. More recent ultramafic rocks have turned out to host mantle noble gases in fluid inclusions trapped from their host magmas or from metasomatising mantle fluids. Not only helium, but also mantle neon and argon are preserved with astonishingly low contamination by atmospheric noble gases. We plan to apply established stepwise crushing noble gas extraction that largely minimises interference of in situ radiogenic and cosmogenic components. In addition, we will apply fluid inclusion microthermometry to identify trails and groups with similar trapping conditions. Individual fluid inclusions or groups can be opened using a laser probe and subsequently analysed by a highly sensitive Noblesse noble gas mass spectrometer especially designed for small sample analyses.

### **Early silicate differentiation of the Isua mantle? Insight from Tungsten isotopes and HSE abundances** Tusch\*, J., et al.

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Interpreting the origin of <sup>182</sup>W anomalies in mafic Archean rocks and the role of a putative missing late veneer [1,2] hinges on tightly constraining the Archean mantle abundances of highly siderophile elements (HSE). However, most HSE estimates for Archean mantle-derived rocks are based on their mafic derivatives, an approach with large uncertainties. Previous <sup>182</sup>W isotope studies did either not include measurements of HSE [2,3] or examined mafic-ultramafic lithologies [4-6], where the ultramafic rocks could not unambiguously be identified as mantle peridotites.

Here, we present the first high-precision W-isotope measurements for > 3.8 Ga old peridotites from Isua that unambiguously show the geochemical characteristics of depleted mantle harzburgites or associated dunites. On average, these mantle peridotites exhibit resolvable but within error uniform excesses in <sup>182</sup>W of around +14 ppm. The observed absolute abundances and ratios of the PGE (Os, Ir, Ru, Pd, Pt), have previously shown to equal those of modern mantle peridotites [7], arguing against a missing late veneer component in these rocks. Additional high-precision W-isotope measurements for other Isua lithologies (Felsic Formation, ultramafic Lens A, Ameralik dikes, TTG, Amphibolites) reveal a uniform <sup>182</sup>W excess of +13 ppm (±1 ppm, 95% conf. limit) for Eo- to Paleoarchean samples (N=26), which is in accord with previous studies [2,5-6]. However, up to more than two orders of magnitude enrichment of W in many samples relative to similarly incompatible elements like Th argue for selective W mobilization. We demonstrate that this vigorous overprint of the elemental W budget in Isua obscures the origin of <sup>182</sup>W isotope anomalies and complicates their use as an indicator for Early Earth processes.

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**Biogeochemical reconstruction of microbial habitats during stromatolite formation using REE and Cd isotopes** Viehmann\*, S., Hohl, S.V., Krämer, D., Walde, D.H.G., Galer, S., Jiang, S.-Y., Meister, P. \*Department für Geodynamik und Sedimentologie, Althanstr. 14, 1090 Wien, Austria Sebastian.viehmann@univie.ac.at

Ancient stromatolites mainly consist of authigenic carbonate which may have formed within living microbial mats and, hence, provide unique archives of local physico-biogeochemical conditions within the mats and of the prevailing water chemistry of the paleo-depositional environment. In this study we report trace element and Cd isotope data of individual mesobands of Late Mesoproterozoic domal stromatolites and conophyta from the Paranoá Group (Brazil). Carbonate leachates of domal stromatolites show rather flat shale-normalized REY patterns (subscript SN) with slightly positive Y<sub>SN</sub> anomalies indicating that the carbonate was formed in a lagoonal environment dominated by fresh water with occasional seawater influence. In contrast, conical conophyta with typical seawater-like REY<sub>SN</sub> patterns formed in a milieu dominated by open ocean seawater. The lack of positive Eusn anomalies suggests that the (sea)water present at both locations was not significantly influenced by high-temperature, hydrothermal fluids, while negative CesN anomalies indicate slightly oxidizing conditions in the atmosphere-hydrosphere system during the Late Mesoproterozoic. In combination with redoxsensitive trace elements such as Ce, Mn and U, the additional analysed  $\varepsilon^{112/110}$ Cd values (see contribution of S. Hohl, this meeting) can be used to clearly distinguish between two carbonate endmembers that formed at the seawater-microbial mat interface and the interior of the ancient microbial mat, respectively. Hence, the geochemical reconstruction of stromatolite environment suggests that REY geochemistry in stromatolite-associated carbonate is a reliable proxy to reconstruct the physico-chemical conditions in Precambrian microbial habitats and further highlights Cd isotopes as novel geochemical proxy to gather unique insights into microbial habitats and element cycling on Early Earth.

#### The role of ammonia for biomolecule synthesis on meteorite parent bodies

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Organic matter (OM) in petrologic type 2-3 carbonaceous chondrites, e.g., Renazzo (CR) or Murchison (CM), mostly consists of large polymerized CHON-bearing molecules with aliphatic and aromatic domains [e.g., 1]. This extraterrestrial OM has long been recognized to play an important role for delivery of biorelevant molecules such as amino acids and sugars to the early Earth. However, the nebular and asteroidal processes that synthesized respective biomolecules and compositions of possible precursors are still largely unknown. Here we investigated isotopic compositions, functional chemistries, and petrographic contexts of several organic grains in carbonaceous chondrites on a submicron scale (NanoSIMS-TEM-EELS), mainly in the carbonaceous chondrite Renazzo. The OM of this meteorite exhibits highly complex irregular, globular or layered morphologies and is commonly intergrown with nanocrystalline phases typical for fluid reactions such as sheet silicates and carbonates. These textures already indicate that any precursor OM in even very pristine CRs was modified in complex chemical settings, above all on the parent body by fluid reactions [2]. Carbon functional chemistry of organic grains confirms the presence of polycyclic aromatic units combined with C-O bonding environments (ketone, aldehyde) as detected in other OM [1], but the nitrogen functional chemistry is more difficult to discern due to low N/C ratios (usually <0.1). In two globular grains from Renazzo, we could document a distinct N-K edge fine structure indicating amino (NHx-) functional chemistry (absorption energy 402.1-402.6 eV) or possibly Nheterocycles, which are important precursors of nucleobases. The globular texture and strong aromaticity indicate a fluidrelated formation origin. Strecker-type reactions are known to synthesize amino acids from ketone or aldehyde precursors and are facilitated by the presence of soluble ammonia moieties in the fluid [3]. Anomalous amino (<sup>15</sup>NH<sub>x</sub>-) aqueous chemistry has therefore likely played an important role for biomolecule synthesis within meteorite parent bodies.

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#### Early Earth mantle heterogeneities - an isotope perspective

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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. These play an essential role in establishing and sustaining the global material cycle, such as for carbon and sulphur (see proposed SPP 1833 project by Hoffmann et al.). Yet, how and when modern-style mantle convection evolved within the first billion years after the accretion of the Earth remains enigmatic. The study of early mantle convection is intertwined with a basic understanding of core formation in a rather peculiar way: Separation of metallic melt from a silicate magma ocean during core formation caused an almost quantitative transfer of so-called siderophile elements from the mantle into the core (e.g. [1]) leaving a diagnostic isotopic signature in the earliest rocks that formed on Earth [2-4]. Yet, shortly after core formation was completed, the Hadean Earth was struck by a limited number of cataclysmic meteorite impacts (e.g. [5]) that injected a small amount of fresh sideropile elements into the mantle, thus partly replenishing their abundances in the silicate Earth [6,7] and implanting an intrinsic isotopic signature into the Earth's mantle. Here, we will be using this planetary-scale tracer experiment to shed light on the internal isotopic heterogeneity of the Early Earth by trying to identify, how this meteoritic material mixed into the Earth's mantle over a timescale of about 1 billion years [8,9]. We will start by analysing the oldest rocks on Earth in order to characterise the isotopic signature that core formation imparted on the isotopic composition of siderophile elements in the mantle before the meteoritic material was completely homogenised. We will then analyse rocks from crucial time periods throughout Earth's earliest history to see, over which timescales the newly arrived siderophile elements were mixed into the Earth's mantle. Our findings, together with complementary results of related projects already funded by – or proposed for the current SPP 1833 call (in particular Münker et al., Rubie et al., Peters et al., Fischer-Gödde et al.), will thus enable a much better and more detailed characterisation of the evolution of Early Earth mantle convection.

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#### Towards melting relations in the MgSiO<sub>3</sub>-FeO+SiO<sub>2</sub> system at lower mantle conditions from multi-anvil experiments

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During crystallization of the terrestrial magma ocean, phase relations for bulk silicate Earth composition govern the dynamic regime of the solidifying portion of the mantle. The phase on the liquidus, i.e., the mineral that first crystallizes from the melt, is of particular importance, as it determines the density balance between silicate liquid and the forming crystallites, as well as the initial temperature profile in the mantle when its dynamic regime transitions from turbulent to solid-state convection. Phase relations in the MgO-SiO<sub>2</sub> system have been explored by multi-anvil experiments [1] and computations [2] up to pressures of the Earth's lower mantle, but the influence of FeO on the phase relations is not sufficiently explored to date. Based on limited work on peridotite composition [e.g., 3], FeO is expected to (i) lower the liquidus temperature and (ii) partition into the melt, strongly affecting the density difference between the melt and mineral phase on the liquidus.

In the current project, we have started to investigate these two aspects in a series of multi-anvil experiments along the MgSiO<sub>3</sub>-Feo+SiO<sub>2</sub> compositional join at 25 GPa, i.e., pressure at the top of Earth's lower mantle. Initial experiments have been performed for Mg<sub>0.9</sub>Fe<sub>0.1</sub>SiO<sub>3</sub> and Mg<sub>0.8</sub>Fe<sub>0.2</sub>SiO<sub>3</sub> samples, with bridgmanite as the phase on the liquidus (Figure 1). We have been able to bracket the liquidus temperature from experiments and determine the equilibrium constant for FeO-partitioning between the coexisting liquid and solid. Partitioning data reveal a strong preference for FeO to remain in the liquid phase, driving the melt composition toward the eutectic point, where the melt should coexist with a phase assemblage of bridgmanite +FeO+SiO<sub>2</sub>.



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Figure 1: Back-scattered electron image of a recovered multi-anvil capsule with  $Mg_{0.9}Fe_{0.1}SiO_3$  composition heated to 2800 K at 25 GPa. The sample has experienced partial melting due to a small temperature-gradient, with typical melt quench texture on the left side. The melt coexists with bridgmanite (dark field on the right side) showing that for the composition invesitgated bridgmanite is the phase on the liquidus.

#### Cadmium stable isotope fractionation during evaporation and recondensation at atmospheric pressure

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Metal stable isotope effects due to evaporation and condensation are of relevance e.g. in cosmochemistry, volcanology and environmental studies. Here, we evaluate the Cd stable isotope fractionation associated with evaporation and condensation at atmospheric pressure. To this end, we determined the Cd isotope compositions of melt residues and condensates from a tube furnace experiment [cf. 1], where Cd was evaporated from stirred anorthite-diopside melts at approx. 1580 K, into air or into a CO-CO<sub>2</sub> mixture at a log $fO_2 = -11.3$ . The Cd vapor recondensed onto Al<sub>2</sub>O<sub>3</sub> plates. These were analyzed for their Cd distribution using an XRF scanner, while Cd isotope analyses were carried out on leachates from these condensation plates. Kinetic theory predicts fractionation factors for <sup>114</sup>Cd/<sup>110</sup>Cd, corresponding to -3.7‰ (air) and -4.3‰ (CO-CO<sub>2</sub>) for the diffusive transport of Cd vapor away from the melt and for the preferential recondensation of lighter isotopes from these atmospheres due to their higher collision frequencies [e.g. 2]. A Rayleigh model for condensates being indeed enriched in the light isotopes. In contrast, Rayleigh evaporation is characterized by fractionation factors corresponding to -1.17‰ (air) and only -0.15‰ (CO-CO<sub>2</sub>). We suggest that the less significant isotope fractionation during evaporation results from the combination of i) significant back reaction due to frequent collisions with atmospheric molecules on top of the melt layer and ii) advective transport of Cd vapor away from the melt surface.

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