

Abstracts

of the Sixth General Meeting "Early Earth evolution" April 6-8, 2022 Tübingen



All abstracts are given in alphabetical order of the first author

Cadmium isotope dichotomy in Apollo lunar soils

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We present Cd isotope data on Apollo 12 basaltic mare soils and Apollo 16 feldspatic highland soils, as well as Apollo 17 orange glass to investigate the history of the lunar regolith which has experienced intensive gardening due to micrometeorite bombardment and impacts, as well as exposure to galactic cosmic rays. Volatile element depletion is greater in the Moon compared to the Earth. Cadmium, a volatile element with a half-condensation temperature of 652K, can thus provide a means of unravelling the origin and mechanisms of this depletion. In addition to mass-dependent stable isotope variations of Cd, excesses in the ¹¹⁴Cd/¹¹²Cd ratio due to thermal neutron capture according to ¹¹³Cd (n, γ) ¹¹⁴Cd (cross section ~2x10⁴ barns) can be related to the fluence of secondary thermal neutrons produced by interactions with cosmic rays in the upper meter of soil.

The results on Apollo 12 (n=5), Apollo 16 (n=8) and Apollo 17 orange glass (74220) soils show large stable Cd isotope variations ($\varepsilon^{112/110}$ Cd= -27 to +106) and variable Cd abundances (12-290 ng/g). A clear Cd isotope dichotomy is observed in $\varepsilon^{112/110}$ Cd-Cd space where Apollo 12 and Apollo 16 soils define two distinct negative correlations with on average higher Cd contents in Apollo 16 soils. Similarly, the relationships between stable Cd isotopes and the soil maturity index (Is/FeO) display a contrasting behaviour: while the enrichment in heavy Cd isotopes generally increases with increasing soil maturity for Apollo 12 soils, a clear relationship is lacking for the Apollo 16 soils. Likewise, there is a strong correlation between Is/FeO and *n*-capture-induced isotope shifts which are greater in Apollo 16 soils. By comparison, Apollo 17 orange glass is the only sample that displays a light Cd isotope signature, has highest Cd abundance and lacks a *n*-capture effect, consistent with its immature state.

We interpret the differences in *n*-capture effects in Apollo 12 and Apollo 16 soils as partly controlled by the duration of cosmic ray exposure near the surface and likely as reflecting their distinct chemical composition with a predominant mare basalt component in Apollo 12 and highland anorthosite component in Apollo 16 soils. The remarkable positive correlation between stable Cd isotope composition and the *n*-capture proxy $\varepsilon^{114/112}$ Cd in Apollo 12 soils passes through the BSE composition where the most immature Apollo 12 soil (12033) plots. This result indicates that the large stable Cd isotope fractionation measured in lunar soils is essentially caused by micrometeorite impacts at the regolith surface. Importantly, 12033 contains a large KREEP component [1] reflected by higher trace elements abundances compared to other Apollo 12 soils analyzed (Wombacher, unpub.). Taken together, our new results may suggest that the Moon and Earth share a similar Cd isotope signature which bears important implications on the lunar and terrestrial volatile elements depletion and models of Moon formation. In particular, a Cd isotope similarity of the Earth-Moon would imply Moon formation from a well-mixed vapor disk without significant Cd isotope fractionation imparted by volatiles loss during and following the impact.

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Microbial iron cycling during deposition and diagenesis of Banded Iron Formations

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Banded Iron Formations (BIFs) are marine sediments consisting of alternating iron (Fe)-rich and silica (Si)-rich layers which were deposited between 3.8 to 1.85 Ga during the Precambrian era. BIFs represent important proxies for the geochemical composition of Precambrian seawater and provide evidence for early microbial life [1]. Iron present in BIFs was likely precipitated in the form of Fe(III) minerals, such as ferrihydrite (Fe(OH)₃), either through the metabolic activity of anoxygenic photoautotrophic Fe(II)-oxidizing bacteria (photoferrotrophs), by microaerophilic Fe(II)-oxidizing bacteria, or by the abiotic oxidation of dissolved Fe(II) (i.e. Fe²⁺) by O₂ produced by cyanobacteria. However, the mineralogy found in BIFs today shows not only oxidized minerals such as hematite but also (partially) reduced minerals like magnetite and siderite. This might be due to the presence of ancient dissimilatory Fe(III)-reducers, which were able to re-reduce the Fe(III) in the primary precipitated Fe minerals (Figure 1).



Figure 1: Schematic display of different biotic and biotic processes that lead to the formation of BIFs [2].

Previous research on elucidating the role of microorganisms in BIFs has focused mostly on individual Fe(II)-oxidizing or Fe(III)-reducing biological processes. The combination of these redox processes, however, is critical to understand the interaction of microbiology and geochemistry leading to BIF formation. Our current and future experiments aim at recreating Fe cycling during BIF deposition with a co-culture of marine Fe(II)-oxidizing (oxygen-producing cyanobacteria *Synechoccocus* PCC 7002) and Fe(III)-reducing bacteria (*Shewanella colwelliana*) in the presence of different iron and silica concentrations. These experiments and the resulting data will allow to discern processes occurring during the deposition and diagenesis of BIFs and better interpret early Earth conditions [1,2]. Here, we show first results from the cycling experiments, which reveal the mineral assemblages that can be formed under such conditions that mimic processes in marine sediments of the early Earth.

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- [3] Schad, M. et al. (2019) Free Radic. Biol. Med., 140, 154-166.

Trace Metal Scavenging in the Early Oceans: Are Hydrogenetic Fe-Mn Crusts Modern Analogues for Precambrian BIFs? Ernst*, D., Schier, K., Garbe-Schönberg, D., Bau, M. *Jacobs University Bremen, Campus Ring 1, D-28759 Bremen, Germany

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Precambrian banded iron formations (BIFs) are widely used as geoarchives for proxies for the physico-chemical evolution of the Early Earth's atmosphere and oceans. While Ge and Si (e.g., Ge/Si ratio, Ge isotopes, Si isotopes) may be used as source and temperature proxies and as indicators for ancient climatic conditions, the Ga-Al may also have potential to be utilized as a source proxy. A prerequisite for the successful application of geochemical proxies to Precambrian sample sets, however, is a thorough understanding of their behaviour in modern systems. Hydrogenetic Fe-Mn crusts and nodules are marine oxidic Fe and Mn precipitates that are sometimes considered modern analogues of Precambrian BIFs. We studied the Ga-Al and Ge-Si systematics in such hydrogenetic Fe-Mn crusts from the Central Pacific with HR-ICP-MS. Our results reveal fractionation of the Ga-Al and Ge-Si element pairs during scavenging by marine Fe-Mn crusts and nodules [1, 2]. While their Ga/Al ratios are lower than those of seawater, their Ge/Si ratios are higher. Mixing calculations indicate that the Ga-Al and Ge-Si fractionation observed in the marine environment are similar to what is observed during continental weathering in the terrestrial environment, suggesting that the chemical speciation of these elements in seawater is not a parameter that controls Ge-Si fractionation during sorption onto Fe and Mn (oxyhydr)oxides. It appears that with regard to trace metal scavenging from seawater, modern hydrogenetic Fe-Mn crusts and nodules are poor analogues of Precambrian oxide-facies BIFs, similar to what is known for REE and Y.

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The Archean rock record of late accretion - New constraints from highly siderophile elements

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Highly siderophile elements (HSE) are key elements for studying core formation and late accretion processes on planetary bodies. Recent isotopic investigation of the highly siderophile element ruthenium (Ru) in Archean ultramafic rocks provided new insights not only into the nature and origin of the materials that were added to the Earth as a late veneer, but also about the timescales and efficiencies of mixing the late veneer into Earth's mantle [1].

Based on evidence from 182W and HSE concentrations previous studies proposed that Archean rocks from southwest Greenland (3.8-3.7 Ga) and the Pilbara craton in NW Australia (3.5-3.2 Ga) derive from mantle sources that did not receive the full complement of late veneer material [2-5]. In this regard, ultramafic rocks from both of these localities display distinct mass-independent Ru isotope compositions with a relative 100Ru excess of 22 parts per million compared with the modern mantle value. The 100Ru excess in these rocks indicates that the Archean mantle source of these rocks already contained a substantial fraction of Ru before the late veneer. The preservation of this pre-late veneer Ru isotope signature requires that Ru was not completely sequestered into the core [6,7] and provides strong evidence that the mantle domains beneath southwest Greenland and Pilbara had not yet fully equilibrated with the late veneer. In contrast to 100Ru excesses identified in Pilbara komatiites, cotemporaneous 3.5-3.2 Ga komatiitic melts from the Dwalile Greenstone remnant in the Kaapvaal Craton (southern Africa) were found to have 100Ru values indistinguishable from the modern mantle [8]. The lack of 100Ru isotope anomalies in these rocks would suggest that the Dwalile mantle source already fully equilibrated with the late veneer by convective mixing.

It would be expected that towards the end of the Archean eon, the transition from a stagnant lid mode to a plate tectonic regime with deep reaching subduction and crustal recycling would have caused efficient mixing of the late veneer component, resulting in a homogenous modern mantle composition as reflected by the homogenous Ru isotope composition of post-Archean mantle-derived rocks [9]. However, even younger 2.7 Ga old Archean komatiites from Kambalda (W-Australia) still exhibit 100Ru excesses [10], indicating that the Kambalda mantle source remained isolated and did not equilibrate with the late veneer component for a prolonged period of time. In summary, Ru isotope data obtained for Archean komatiite formations from Australia (Pilbara and Kambalda) and southern Africa (Dwalile) reflect different time scales for mixing of the late veneer component into the Archean mantle. The Archean mantle was not well mixed with respect to accretionary isotopic signatures as indicated by more variable 100Ru isotope anomalies in comparison to the homogenous composition of the modern mantle.

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- [3] Willbold et al. (2011) Nature.
- [4] Tusch et al. (2019) GCA. [5] Tusch et al. (2021) PNAS.
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On the trail of oxygenic photosynthesis in ancestral Cyanobacteria on early Earth

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While oxygenation of the atmosphere on early Earth is attributed to cyanobacterial oxygenic photosynthesis, the limitations on their expansion is not well understood. Our worked is focussed on assessing the impact of early Earth conditions on ancestral lineages of Cyanobacteria. Iron is essential for photosynthetic pigment biosynthesis, however the high availability of iron on early Earth contrasts the present day scenario. We have recently investigated the evolution of iron uptake receptors across the Cyanobacteria and identified that commonly occurring uptake mechanisms only arrived in the current lineages during the Proterozoic. This implies that the less efficient generic divalent cation receptors for zinc and cobalt, as well as siderophore uptake, may have been used to satisfy the high iron needs of early Cyanobacteria during the Archean. The release of oxygen provides stress on the biochemical process within the bacteria as it results in the generation of oxygen free radicals. Our research in a simulated marine environment demonstrates that modern-day deep branching Cyanobacteria undergo less oxidative stress under an anoxic atmosphere than under present day atmospheric conditions. Additionally, we demonstrate increased O2 accumulation for aquatic cultures of Cyanobacteria under a 24-hour diurnal cycle compared to a half day cycle. In summary, our research to date suggests that reduced iron acquisition efficiencies may have limited the spread of Cyanobacteria on early Earth, while oxidative stress does not appear to have been a limiting factor. Further investigations into the role of iron bound to heterotrophic organic ligands under anoxic conditions would further elucidate the conundrum of iron limitation in a ferruginous world.

Decoding the marine oxygenation state across the GOE – preliminary δ^{98} Mo data from the Duitschland/Rooihoogte Formation (South Africa)

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The ~2342±18 Ma [1] to 2316±7 Ma [2] old Duitschland/Rooihoogte Formation in the Transvaal Basin (South Africa) is deposited at a critical time interval in Earth's history, just at the beginning of the Great Oxidation Event (GOE), and has thus been important in terms of understanding the processes that lead to the first appearance of atmospheric oxygen [3, 4, 5]. However, most studies of the Duitschland/Rooihoogte Formation targeted the loss of mass-independent fractionation of sulfur isotopes (MIF-S) and thus the initiation of a slightly oxygenated atmosphere, while little attention has been directed towards the oxygenation state of the contemporaneous marine realm. The CIMERA Agouron GOE and Biomarker Drilling Project provides four drill cores intersecting the Duitschland/Rooihoogte Formation at different distances to the paleoshoreline, which enable us to establish a three-dimensional model of the oxygenation state of the marine ecosystem in the Transvaal Basin at the beginning of the GOE. Data from all four drill cores suggest a predominantly suboxic to oxic water column throughout the deposition of the Duitschland/Rooihoogte Formation. This observation is most pronounced in redox-sensitive trace elements (Mo, U), which consistently and independently of methods applied [6, 7] indicate a deposition in a suboxic to oxic environment. Preliminary δ^{98} Mo data from one proximal and one distal core show a shift from consistently light to steadily heavier δ^{98} Mo_(NIST+0.25%) values towards the top in both cores. We attribute this to the deposition of more Fe-rich (and Mn-poor) sediments towards the top of the cores along with the initiation of H₂S production by sulfate reducing bacteria in the sediment pore waters leading to increased, although not sulfidic, dissolved H₂S concentrations. Both processes would push δ^{98} Mo compositions of shales towards heavier values compatible with the observed δ^{98} Mo_(NIST+0.25%) changes [8]. The role of both processes operating at the time of deposition are indicated by the positive correlation of Fe/Mn, total sulfur and δ^{98} Mo_(NIST+0.25%) with stratigraphic height. Our preliminary data suggest that the Duitschland/Rooihoogte Formation was deposited under suboxic to even oxic conditions on a basin wide scale.

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BASE: Eight boreholes and three tunnels through 3.5 km of Early Archean shallow-water strata investigate the setting of early life

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The up to 3.5 km thick Moodies Group (ca. 3.22 Ga) of the Barberton Greenstone Belt, South Africa and Eswatini, exposes some of the oldest well-preserved sedimentary strata on Earth. Strata were deposited within only a few million years in prodeltaic to alluvial settings, with a dominance of tidal deltas and coastal plains; they provide a very-high-resolution record of Early Archean surface conditions. Widespread microbial mats, early diagenetic vadose-alteration zones and tidal rhythmites are common. Moodies strata provide a unique opportunity to investigate the conditions under which bacterial life spread and thrived on early Earth. The ICDP *Barberton Archean Surface Environments* (BASE) Project is currently (Nov., 2021 – May, 2022) drilling eight inclined boreholes of ca. 300-450 m length through steeply inclined or overturned sedimentary (and minor volcanic) strata at selected sites of the Moodies Group; data are complemented by sampling in three long tunnels. Currently, three rigs are operating. Thirty to sixty m of high-quality core is daily processed in a large, publicly accessible site in downtown Barberton by a team of nine. An exhibition provides background for visitors and relates this fundamental geoscience research to the Barberton Makhonjwa Mountains World Heritage Site. As of the time of writing, three boreholes are completed and all drilling targets had been met.

Reassessing evidence of Moon–Earth dynamics from tidal bundles at 3.2 Ga (Moodies Group, Barberton Greenstone Belt, South Africa)

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Past orbital parameters of the Moon are difficult to reconstruct from geological records because relevant data sets of tidal strata are scarce or incomplete. The sole Archean data point is from the Moodies Group (ca 3.22 Ga) of the Barberton Greenstone Belt, South Africa. From the time-series analysis of tidal bundles from a well-exposed subaqueous sand wave of this unit, Eriksson and Simpson (2000) (1) suggested that the Moon's anomalistic month at 3.2 Ga was closer to 20 days than the present 27.5 days. This is in apparent accordance with models of orbital mechanics which place the Archean Moon in a closer orbit with a shorter period, resulting in stronger tidal action. Although this study's detailed geological mapping and section measuring of the site confirmed that the sandstone bed in question is likely a migrating dune, the presence of angular mud clasts, channel-margin slumps, laterally aggrading channel fills and bidirectional paleocurrents in overlying and underlying beds suggests that this bedform was likely located in a nearshore channel near lowerintertidal flats and subtidal estuarine bars; it thus carries risk of incomplete preservation. Repeated measurements of foreset thicknesses along the published traverse, measured perpendicular to bedding, failed to show consistent spectral peaks. Larger data sets acquired along traverses measured parallel to bedding along the 20.5 m wide exposure are affected by minor faulting, uneven outcrop weathering, changing illumination, weather, observer bias and show a low reproducibility. The most robust measurements herein confirm the periodicity peak of approximately 14 in the original data of Eriksson and Simpson (2000). Because laminae may have been eroded, the measurements may represent a lower bound of about 28 lunar days per synodic month. This estimate agrees well with Earth-Moon dynamic models which consider the conservation of angular momentum and place the Archaean Moon in a lower orbit around a faster-spinning Earth.

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Constraining ⁶⁰Fe-abundance in the early Solar System using in situ analysis of pristine chondritic material

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The short-lived (t¹/₂ \approx 2.6 million years) radioactive isotope ⁶⁰Fe may have had a role as a heat source in the thermal evolution of some of the earliest planets of our Solar System. The initial Solar System abundance of the isotope was estimated by [1] to have been about 10^{-8} of the abundance of ⁵⁶Fe, based on the Fe-Ni isotope composition of bulk angrites, eucrites, and chondrules. In situ Fe-Ni isotope analysis of chondrules and troilites first suggested that the initial abundance of ⁶⁰Fe might have been orders of magnitude higher [e.g., 2,3], but recent in situ measurements cast doubt on the validity of the latter abundance estimates [4-5]. In addition to this, there are bulk and in situ isotope data indicating that the carbonaceous chondrite-like (CC) and non-carbonaceous (NC) isotope reservoirs may have had distinct ⁶⁰Fe/⁵⁶Fe ratios [e.g., 6]. At the Meeting we present the results of additional in situ, high spatial resolution Fe-Ni isotope measurements using the NanoSIMS (primary O⁻ beam diameter 200–300 nm), to further constrain the initial ⁶⁰Fe/⁵⁶Fe ratio of the Solar System and the potential difference between the ⁶⁰Fe-abundances of the CC and NC isotope reservoirs. We analysed troilites and chondrule silicates from petrologic type 3 ordinary (Semarkona, MET 00526, QUE 97008, NWA 8276), and carbonaceous chondrites (ALHA77307, DOM 08006). Anomalies in ⁶⁰Ni/⁶²Ni ratios are usually solar within the 95 % confidence intervals ($\pm 2\sigma$; 6 out of 86 troilite-, and 3 out of 76 silicate measurements yielded anomalies > 2σ), and could be explained by stochastic variations. When silicate isotope data are combined, an average initial ⁶⁰Fe/⁵⁶Fe ratio of 3.76 (\pm 4.69) × 10⁻⁸ can be calculated. Troilites show a similar picture, with the average inferred initial ⁶⁰Fe/⁵⁶Fe ratio being 1.05 (\pm 1.48) × 10⁻⁸. Transmission electron microscopy of three sulfides and three chondrules revealed no sign of alteration at the isotope analysis spots. The Fe/Ni ratios and Ni isotope compositions of the analysed phases probably remained undisturbed since formation. Our data further confirm the lower abundance estimates for ⁶⁰Fe in the early Solar System [1].

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Tungsten (isotope) cycling in modern marine basins and implications for paleoredox reconstructions

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The stable tungsten (W) isotope composition of modern seawater ($\delta^{186/184}$ W = +0.543 ± 0.046 ‰; [1]) is markedly heavier than the main input source of marine W, the upper continental crust ($\delta^{186/184}$ W of +0.080 ± 0.053 ‰; [2]). In analogy to Mo, the driving mechanism for this isotopic difference is the preferential adsorption of isotopically light W onto manganese (Mn) oxides in (hyp)oxic marine settings. Therefore, temporal changes in the seawater stable W isotope composition might be linked to the areal extent of (hyp)oxic conditions. The rise of marine oxygen concentrations in Earth's history would shift the seawater $\delta^{186/184}$ W towards higher values. However, the application of stable W isotopic compositions as a new paleoredox proxy requires a better understanding of stable W isotope fractionation during sediment deposition and diagenesis and the identification of sediments that preserve temporal trends in the $\delta^{186/184}$ W of seawater.

Here we present stable W isotope data for sediments from the Landsort Deep in the Baltic Sea [2]. In this basin redox stratified conditions with hypoxic or euxinic bottom waters repeatedly alternated with fully oxic conditions during the last ~1,700 years. During long-lasting fully oxic periods the detrital component controls Mn and W abundances in the sediments leading to crust-like $\delta^{186/184}$ W values between -0.008 and +0.112 ‰. During periods of bottom water hypoxia sediments are authigenically enriched in Mn and W showing higher $\delta^{186/184}$ W values up to +0.226 ‰. Smooth depth trends in $\delta^{186/184}$ W during hypoxic phases ultimately mirror temporal changes in the inflow intensity of O₂ bearing Baltic seawater. High inflow rates enhance the shuttling of Mn oxides that preferentially scavenge isotopically light W. As a consequence, the $\delta^{186/184}$ W of residual bottom waters and subsequently formed sediments increases. Therefore, temporal variation in sedimentary $\delta^{186/184}$ W values is linked to the extent of Mn oxide formation that in turn depends on changing marine redox conditions. This relationship highlights that stable W isotopes are a promising new proxy for the reconstruction of marine redox conditions in early Earth history.

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Nitrogen isotope systematics of inorganic N-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. Chondritic meteorites contain small quantities of various nitrides. Si3N4, TiN, and sinoite (Si2N2O) are common accessory phases of enstatite chondrites (ECs). Nitrides in ordinary (OCs) and carbonaceous chondrites (CCs), however, have been scarcely reported [e.g., 1–7]. Another N-carrying phase that occurs occasionally in chondritic meteorites are graphite inclusions [e.g., 8]; however, their abundances are not well constrained.

We found that the average N-isotopic compositions of nitrides (Si3N4, TiN, CrN, and Fe4N) from CCs and ECs [9] differ significantly, and we also observe variations between different CC groups. Nitrogen becomes isotopically heavier in nitrides from EC-(OC-) through CM, CV&CO to CR-CH&CB chondrites. This may indicate increasing amounts of outer Solar System N in the respective reservoirs of nitrides, and could reflect different heliocentric distances of the formation regions [e.g., 10]. However, we also observe that the N-isotopic compositions of nitrides are sometimes significantly different from those of their host meteorites and meteorite groups [e.g.,9,11]. In addition, graphite in ECs shows heavier N-isotopic compositions than the EC-nitrides. This suggests several different N reservoirs and/or different formation/alteration pathways for the various N-carriers within a given meteorite group. and could also explain the bulk N-isotopic variations observed for, e.g., the OCs [12].

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Sulfur and hafnium isotope constraints on depletion and refertilization history of Eoarchean mantle peridotites

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Remarkably well preserved Eoarchean peridotites found in the Itsaq Gneiss Complex (IGC) of southern West Greenland have been subject to extensive study, including petrographic, bulk composition, and trace element analysis. The geodynamic history of these rocks and the processes that brought about their formation, however, remain controversial. Some researchers have argued that these rocks represent the oldest slivers of Earth's mantle, emplaced in the crust by a modern-like horizontal tectonic process and recording a history of hydrous melt depletion and refertilization. Others have argued that they are ultramafic cumulates and have their origins in nonuniformitarian, vertical tectonic processes. Here, we present multiple sulfur isotope data pointing to the introduction of surface-derived material into these rocks during the Archean, indicating an early onset of crustal recycling similar to modern plate tectonics. Furthermore, correlations between mass-independent $\Delta 33S$ signatures in these rocks with existing major, trace element abundance, and eHf data indicate that these peridotites record episodes of hydrous melt depletion and re-enrichment by a percolating melt with a highly depleted mantle source that already existed in the Eoarchean. These correlations strongly support the Archean origins of positive eHf signatures already found in these rocks, as well as the existence of depleted mantle domains forming on Earth as early as the Hadean. The correlations between sulfur isotope and other data in these peridotites are best explained by an Eoarchean mantle origin, and modification by processes consistent with those in a mantle wedge in a modern subduction-like setting.

The reliability of microbialites as archives for reconstructing the redox state of seawater using U isotopes: a summary Martin^{*}, A. N. and Weyer, S.

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Microbialites form at the interface with the atmosphere in shallow-water environments, rendering them ideal archives of redox-sensitive, non-traditional isotope systems, such as uranium (238U/235U). Thus, U isotope signatures of microbialites can considerably improve our understanding of Earth's oceanic and atmospheric oxidation. However, microbial redox cycling of elements such as U may yield further isotope fractionation, complicating interpretations of isotopic signatures. Such interpretations will be further complicated if a distinct isotopic offset is associated with particular microbial communities found in certain environments. The most common depositional environments that host Archean stromatolites are open marine, semi-restricted marine and volcanic rifts. Here we present δ^{238} U values and trace element composition of a range of modern microbialites to assess the (bio)environmental impact on their U isotope signature. Modern stromatolite crusts in the hypersaline, restricted marine embayment of Shark Bay, Western Australia exhibited a δ^{238} U offset of ca. +0.1‰ from seawater whilst deeper and older stromatolite laminae exhibited offsets up to +0.4‰. Microbial mats from the open marine setting of Schiermonnikoog, a barrier island in the North Sea, reliably recorded seawater-like δ^{238} U values (ca. -0.4‰) when the authigenic U fraction was selectively leached. Conversely, volcanic rift microbialites from Lake Chew Bahir produced a wide range of δ^{238} U that were both above and below the value of modern lakewater (ca. -0.3‰), indicating enhanced redox cycling of U. Thus, the local environment appears to exert a strong control on microbialite δ^{238} U, which is independent of the atmospheric redox state. These results highlight the need to carefully interpret the depositional environment of Precambrian stromatolites when applying paleoredox proxies, particularly in ancient volcanic rifts.

¹⁸²W variations in the Paleo-Archean Kaapvaal and Singhbhum Craton: Implications for the extent of Hadean mantle heterogeneity

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Through the decay of the short-lived radionuclide ¹⁸²Hf to ¹⁸²W and the fractionation of parent/daughter isotopes, small variations in the isotopic composition of W can be established in Hadean mantle reservoirs. Excesses in ¹⁸²W in Eo-Archean rocks are commonly attributed to either incomplete mixing of 'Late Veneer' material into the mantle [1] or the fractionation of parent and daughter isotopes during silicate and/or metal fractionation within the first 50 Ma years after solar system formation [2]. On a global scale, the pervasive ¹⁸²W excess found in Eo-Archean terranes is diminished in Paleo-Archean rocks from ca.3.5 Ga onward. This observation is commonly attributed to progressing convective homogenization of the mantle [1], [3], [4]. Nevertheless, some Hadean mantle domains appear to have survived past the Paleo-Archean [5], offering a unique opportunity to study the intricate geodynamic conditions of the Earth's young mantle at the possible onset of plate tectonic processes [6].

The Paleo-Archean Onverwacht Group of the Kaapvaal Craton in South Africa features a unique disparity of W isotope compositions: Negative μ^{182} W variations in the 3.55 Ga old Schapenburg Greenstone Remnant [7] are contrasted by modern mantle μ^{182} W values of about zero in slightly younger rocks of the 3.45 Ga old Komati formation [2]. The Indian Singhbhum Craton, on the other hand, features similar Greenstone sequences and ages as the Kaapvaal Craton. In particular, the Badampahar Group exposed in the Daitari Greenstone Belt. However, no W isotope data is available for the Daitari sequence. As such, existing age and isotope data as well as geological similarity between both cratons make them prime targets to assess the temporal and geographical extent of W isotope anomalies in the Archean mantle. Accordingly, we analyzed the ¹⁸²W and ¹⁴³Nd isotopic along with major and trace element compositions of a suite of felsic and mafic rock samples from the 3.55 to 3.53 Ga old Sandspruit and Theespruit formations, the lowermost stratigraphic units of the Onverwacht Group as well as the mafic to ultramafic samples from the > 3.51 Ga old Kalisagar Formation of the Badampahar Group . For the Onverwacht dataset, our results indicate a heterogeneous ¹⁸²W composition, shifting towards negative μ^{182} W anomalies similar to those found for komatiites of the Schapenburg Greenstone Remnant. Preliminary W isotope analyses of the Kalisagar Formation reveal no resolvable ¹⁸²W anomalies, suggesting the absence of an Hadean mantle component. The W isotope data for both studied regions agree with the evidence of a globally progressing mantle homogenization in the Paleo-Archean mantle and document a highly heterogeneous mantle in terms of Hadean components.

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Are the world's oldest postulated eolian sandstones (Moodies Group, Barberton Greenstone Belt, 3.2 Ga) truly eolian? Reimann, S. 1,*, Zametzer, A., 1,2, Heubeck, C., 1

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It is unresolved when eolian (sediment transport by wind) processes began to significantly affect global mean sand composition and texture through abrasion and improved sorting because evidence of eolian textures and sedimentary structures from the early geologic record is poor and ambiguous. We found no reliable petrographic or textural indicators of eolian processes, argued by Simpson et al. (2012) to be the oldest evidence of such, from well-preserved strata of the up to 3.6 km-thick Moodies Group (ca. 3.225-3.215 Ga) in the Barberton Greenstone Belt, South Africa. Our subsequent investigation of four comparable, compositionally and texturally mature Moodies Group sandstones with large foresets also failed to produce convincing compositional, textural, and facies evidence of eolian depositional environments although the inferred coastal-floodplain and estuarine depositional environments may have been hospitable to eolian processes. Sandstones in most investigated locations are generally too coarse (mean grain diameter ca. 600 µm), only moderately to poorly sorted, and too positively skewed to be of eolian origin, compared to recent examples. Foresets commonly also show shale laminations, granules, and rare pebbles. Nevertheless, we cannot exclude the possibility that a proportion of the investigated strata may have experienced eolian transport, perhaps under nonuniformitarian conditions. Thus, the significance of eolian processes on early Earth and their potential contribution to the high degree of textural and compositional maturity of early Archean quartzarenites remains largely unknown.

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Exploring the geobiology of ancient hydrothermal sulfides - a multidisciplinary approach to early life on Earth

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Hydrothermal sulfide systems are among the most ancient habitats on Earth and are widely considered as candidate sites for the emergence of life. Deposits from such settings are thus of great evolutionary significance, but the geobiology of our planet's most ancient hydrothermal sulfides remains largely unexplored. This is most likely due to a limited understanding of the formation and preservation of microbial biosignatures in such settings, particularly over geological timescales. Here we present our strategy to explore the geobiology of ancient hydrothermal sulfides by integrating analytical and experimental methods from geology, geochemistry, and microbiology. More specifically, we experimentally alter abiotic minerals and microbial precipitates under physical and chemical hydrothermal conditions, and thoroughly characterize the products with analytical imaging techniques, mineralogical methods and geochemical approaches. By comparing the observed characteristics with those of minerals in modern and ancient hydrothermal sulfide deposits, we aim to identify primary biogenic mineral precipitates and their transformation products. This approach will allow us to develop a more robust understanding of the formation and preservation of biosignatures in hydrothermal environments.

Towards making habitable Earth(s): the importance of pre-natal physical and chemical conditions

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

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Outgassing history and early atmospheric processes recorded by palaeoatmospheric noble gases in Archaean rocks Trieloff*, M., Hopp, J., Ott, U.

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The atmospheric ⁴⁰Ar/³⁶Ar-ratio (modern value 298.6, initial value ~zero) has changed with time due to production by decay of ⁴⁰K (half-life = 1.25 Ga) into ⁴⁰Ar, and during degassing of this radiogenic ⁴⁰Ar from solid Earth reservoirs (mantle and crust). Earth's mantle lost a significant share (>95%) of its primordial Ar very early in the first few hundred million years, whereas the degassing of continental crust depended on its volume, as well as tectonic and environmental boundary conditions. Knowledge of the secular change of the atmospheric ⁴⁰Ar/³⁶Ar-ratio thus can set constraints to degassing models. However, potential superposition of crustal gases or in situ radiogenic nuclides (e.g., ⁴⁰Ar) complicates identification of potentially retained ancient atmospheric noble gases in old rocks.

In this study, we examined the noble gas composition of Neoarchean carbonate successions from the Transvaal Supergroup (S Africa) deposited in a shallow marine basin, utilizing the stepwise crushing method. Carbonates were affected by silicification during karstification about 2.3 Ga ago, leading to chert formation, and by a mild hydrothermal overprint in the northeastern part of the basin in course of the Bushfeld activity 2 Ga ago. Analyses of 3 dolomite and 3 chert whole rock samples revealed linear relations in 40 Ar/ 36 Ar vs 4 He/ 36 Ar isotope space that point to a mixture of atmospheric gases, in situ radiogenic 4 He and 40 Ar* and crustal excess 40 Ar. However, in case of one dolomite and one chert we observed well-defined correlations that correspond to mixtures of ancient atmosphere with in situ radiogenic 40 Ar and 4 He, reproduced with analyses of duplicates. The respective 40 Ar/ 36 Ar-ratio in the hydrothermally affected dolomite is 266±8 (1 σ), which is at the upper range of expected model compositions for 2.0 Ga old atmospheric argon. We regard this value as upper limit as it still could contain minor excess 40 Ar. The two mixing lines obtained for the chert differ in their trapped 4 He/ 36 Ar-ratio defining a 2 σ -range in 40 Ar/ 36 Ar of 120.2 to 238.8. The lower bound would necessitate a major, possibly alteration-related, release of 40 Ar* from solid Earth during the Great Oxidation Event, whereas the upper limit corresponds to model calculations with K(BSE) of 160 ppm and common degassing scenarios.

Recycled roots of Hadean protocrust – A possible OIB endmember?

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In recent models, deficits of ¹⁸²W in modern OIBs are explained by a primordial reservoir in the lower mantle that mixes with classical mantle endmember components DMM, EM1, EM2, and HIMU [1]. Yet the exact origin of the low ¹⁸²W endmember in modern OIBs is not known. Popular models argue that negative ¹⁸²W isotope anomalies originate from core-mantle interaction either by chemical exchange or by isotopic equilibration [2,3]. Alternatively, it is plausible to assume that negative ¹⁸²W anomalies in OIBs could hint at deep-rooted mantle sources that did either not receive the full complement of late accreted material during the late veneer or underwent early silicate differentiation during the lifetime of short-lived ¹⁸²Hf. Understanding the origin of this mantle reservoir and its evolution in the geologic past is of great importance to resolve the ¹⁸²W dichotomy between modern OIBs and most Archean mafic rocks that largely display positive ¹⁸²W anomalies. Notably, Archean rocks from the Kaapvaal Craton, southern Africa, are unique in this regard, as they were shown to be the only known Archean rocks displaying negative ¹⁸²W isotope anomalies. To better understand the origin of these ancient signatures we performed high-precision ¹⁸²W isotope measurements on a wide selection of rocks from the Kaapvaal Craton that were previously analyzed for ¹⁴²Nd [4] and combine our results with constraints from long-lived ¹⁷⁶Hf-¹⁴³Nd-¹³⁸Ce, and trace element systematics to better characterize their parental mantle sources. In order to assess if late accreted material affected ¹⁸²W isotope systematics we also investigated Ru isotope systematics that were recently introduced as a novel tool to decipher the inventory of late accreted material in mantle rocks [5]. All these parameters were then combined to develop a geodynamic model that reconciles all observational constraints. Modern mantle-like Ru isotope compositions in our samples indicate that the Kaapvaal mantle source had already completely equilibrated with late accreted material, thereby ruling out late veneer contributions to ¹⁸²W isotope systematics. We can rather demonstrate that lower crustal Hadean-Early Archean restites from prolonged TTG formation were recycled into the upper mantle and significantly contributed to mafic magmatism in the Kaapvaal Craton. If preserved in the modern mantle, such recycled components may even account for ¹⁸²W deficits in modern OIBs. In this regard, our model constitutes a viable alternative explaining the origin of primordial components in the source region of modern OIBs, thus bridging between ¹⁸²W isotope systematics in Archean mantle derived rocks and their modern-day counterparts.

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Minerals and life - using pyrite as an indicator of microorganisms

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Life has co-evolved with rocks and minerals since its origins 4 billion years ago, shaping the whole ecosystem of our planet. Pyrite (FeS2), being the most abundant iron sulfide mineral, plays a key role in many different biogeochemical cycles on Earth. It comes in different shapes, the most common of which are cubic and unique raspberry-shaped framboids. Framboidal pyrite in particular has been suggested to be formed only in the presence of life – thus, different pyrite morphologies could be used to discern microbial versus abiotic mineral formation in different periods of Earth's history and other habitable worlds. However, biogenic pyrite has rarely been synthesized in laboratory-controlled conditions, giving doubts as to whether the mineral can actually be used as a biosignature.

Here, we describe experiments aimed at forming biogenic pyrite to enable its evaluation as a robust biosignature. We decided to use Desulfocapsa sulfoexigens – an anaerobic and mesophilic marine bacterium that can disproportionate sulfur species to form H2S and sulfate. Sulfur disproportionation is a redox reaction in which inorganic sulfur is both an electron donor and electron acceptor. It is possibly the oldest microbial metabolism of sulfur ranging back to 3.5 Ga, which makes it highly relevant to pyrite formation on the early Earth. We will set up experiments to investigate biogenic pyrite formation by D. sulfoexigens in the presence of different sources of iron (Fe3+, ferrihydrite, goethite, hematite) and sulfur (thiosulfate, elemental sulfur, colloidal sulfur). The mineral products will be investigated through a multilayered approach using culturing, SEM, geochemical and mineralogical analyses (μ XRD, μ Raman). We expect to find framboidal pyrite in our samples alongside other iron sulfide minerals such as greigite and mackinawite. Higher microbial abundance combined with nano-sized Fe and S sources are expected to increase pyrite formation. As a whole, our experiments will result in an optimized protocol for biogenic pyrite formation, which will enable us to evaluate whether pyrite is truly a robust biosignature for life.

Graphitic Inclusions in Zircon from Cambrian Granite: Implications for the Preservation of Hadean Biosignatures

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The Hadean eon is a critical time in that life might have already emerged during the first few 100 million years of Earth's history. Graphitic inclusions in detrital zircon presently represent the only tangible carbon isotopic record in Hadean materials, which display a $\delta^{13}C_{PDB}$ value of $-24 \pm 5 \%$ interpreted to imply biologic activity already by 4.1 Ga [1]. How graphite became incorporated into magmatic zircon and might have encapsulated isotopic signatures since then, however, remains incompletely understood. The assignment of carbon isotope signatures as distinctly biogenic requires the assessment of processes such as source rock assimilation of C_{org} -rich sediments ($\delta^{13}C_{PDB} = -25 \%$) or graphite precipitation from carbonaceous fluids [2,3] which could lead to $\delta^{13}C$ depletions compared to a mantle source ($\delta^{13}C_{PDB} = -6 \%$). To amend this lack of knowledge, we investigated zircons from the graphite-bearing Rumburk granite and adjacent (meta)sedimentary country rocks of Neoproterozoic to Paleozoic age from the Lusatian complex of the Bohemian Massif [4].

Zircon U-Pb geochronology confirms a Cambro-Ordovician age of the Rumburk granite and magmatic recycling of detrital zircon indicated by inherited Proterozoic zircon cores. Uranium concentrations vary between 70 and 3600 ppm, with generally lower Th/U in zircon rims (~0.05–0.2), attesting to the possible influence of co-crystallizing monazite at low temperature, whereas "old" cores with Th/U >0.2 are of high-temperature igneous origin. $\delta^{18}O_{SMOW}$ values of ~8 ‰ in cores and rims (after zircon chemical abrasion) underscore sedimentary protoliths. The lack of a positive Ce anomaly in most rims in contrast to many cores indicates crystallisation of the rims from a highly reduced melt. The Ti-in-zircon thermometer indicates a crystallisation temperature peak at around ~700°C.

Opaque inclusions in Rumburk zircons identified by micro-Raman predominantly comprise ilmenite and rutile. Carbonaceous phases include graphite and rare calcite. Raman spectra of five graphite inclusions indicate a significant variation in crystallinity, where disordering of the graphite structure might have been caused by radiation damage. Carbon isotopic measurements of graphite were performed at high spatial resolution by SIMS using reference graphite USGS24 ($\delta^{13}C_{VPDB} = -16.049 \pm$ of 0.035‰ [5]; own analyses with a SIMS spot size of ~5 µm diameter, however, indicate heterogeneity of ~0.7‰). Isotopic variations determined for single graphite inclusions range from -36 to -44 ‰, -29 to -40 ‰, -28 to -39 ‰, -20 to -38 ‰, and -8 to -15 ‰.

These results are consistent with assimilation of isotopically light carbon [2] for which the (meta)sedimentary units with bulk $\delta^{13}C_{VPDB}$ values between -21 and -25‰ might be considered as the potential source composition of C in the Rumburk granite. Isotopically heavier values might be caused by mixing with carbon from a mantle-derived fluid. Internal isotopic variations within analysed inclusions can be explained by Rayleigh fractionation during graphite precipitation in voids of porous zircon crystals from mixtures of CO₂ and CH₄-rich fluids [3].

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New U–Pb and *P–T* constraints for the Laxfordian tectono-metamorphic event in the southern and northern regions of the Archean Lewisian Gneiss Complex, NW Scotland: implications for Palaeoproterozoic reworking during Nuna amalgamation

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Despite extensive investigations, the tectono-thermal evolution of the Archean crust in the Lewisian Gneiss Complex, NW Scotland (LGC; Fig. 1) remains poorly constrained. Several U–Pb zircon geochronological and metamorphic studies have focused on the granulite-facies central region, where the oldest, dominant, high-grade metamorphic Badcallian event (8-10 kbar and 900–1000°C; [1]) dated at c. 2.8–2.7 Ga (e.g., [2]) has been overprinted by the amphibolite-facies Inverian (c. 2.5 Ga; e.g., [2, 3]) and Laxfordian (c. 1.9–1.7 Ga e.g., [2, 4]) tectono-metamorphic stages. These retrograde, younger events occurred along crustal-scale ductile shear zones (Fig. 1). Nonetheless, debates remain regarding the nature and timing of the Inverian overprinting event in the central region, due to a continuous spread of apparent concordant U–Pb zircon dates as young as 2.5 Ga, which challenge the discrimination of discrete overprinting events from a protracted high temperature regime. Additionally, the timing and conditions of the Inverian and Laxfordian events in the southern and the northern regions are poorly constrained. In this contribution, we present new petrographic and structural data, combined with U–Pb geochronology of zircon rims in felsic gneisses, U–Pb geochronology of titanite and phase diagrams for amphibolitic samples from the northern and southern regions of the LGC. Our field observations show that potential Badcallian structural relicts are preserved in both regions, which, in turn, have been significantly reworked by NWstriking, steep Inverian fabrics. The latter are pervasively overprinted by co-axial subvertical fabrics that developed under amphibolite-facies conditions (P = 4–6 kbar and T = 630–670°C) during the Laxfordian event dated by in-situ U–Pb titanite geochronology at c. 1.78 Ga and at c. 1.84 Ga in the northern and southern regions, respectively. In contrast, the central region U–Pb zircon rim dates from the felsic gneisses show a dominant Inverian metamorphic overprint at c. 2.5 Ga.

Metamorphic titanite in amphibolitic samples and zircon rims in felsic gneisses from the northern and southern regions often yield Laxfordian dates as young as c. 1.8 Ga. Combined, these results suggest that during the Palaeoproterozoic, the central region of the LGC reflected a low strain domain, where intense deformation and fluid-assisted metamorphism were restricted to crustal-scale shear zones (e.g., LSZ and CSZ in Fig. 1). This less reworked region is bounded by the southern and the northern regions which, in turn, acted as wide, high-strain, likely reactivated, steep belts. accommodating most Laxfordian deformation and fluid circulation. This pervasive Laxfordian event has important implications for the configuration of NW Scotland in relation the to east Nagssugtogidian and the Lapland-Kola orogenic belts in the neighbouring Laurentia and Baltica, respectively, during the amalgamation of Palaeoproterozoic Nuna.

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Organic matter in sedimentary barites from the 3.5 billion-year-old Dresser Formation (Pilbara Craton, Australia)

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It is hypothesized that 3.5 billion-year-old bedded barite from the Dresser Formation (Pilbara Craton, Australia) was formed in an evaporitic hydrothermal caldera environment [1]. Within these barites several primary fluid and solid inclusions are present. The fluid inclusions contain volatiles like H2S, COS, and CS2, as well as simple organic compounds (e.g., acetic acid, organic polysulfanes, thiols). As constituents of Archaean hydrothermal fluids, such compounds may have represented fertile substrates for early life forms [2]. The solid inclusions consist of iron sulfides [3; this study], calcite, dolomite, quartz, anatase, ankerite, and insoluble organic matter (kerogen). The kerogen particles appear either at the edges of single growth zones or within the barite crystals and not in secondary quartz veins, supporting that the kerogen is syngenetic. Preliminary NEXAFS measurements revealed that the kerogen has an aromatic nature. Further experiments are planned to investigate in more detail the structure of the kerogen and the composition of organic compounds trapped in the fluid inclusions (Raman, near edge X-ray absorption fine structure (NEXAFS), catalytic hydropyrolysis (HyPy), liquid-chromatography–mass spectrometry (LC-MS)). Our multi-technique approach will provide an advanced view of the origin of organic components in the 3.5 Ga old barites, broadening our understanding of early life evolution.

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